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PREVENTION REFERENCE MANUAL:
CHEMICAL SPECIFIC
VOLUME 14: CONTROL OF ACCIDENTAL RELEASES OF PHOSGENE

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16. ABSTRACT The report, discussing phosgene, is one of a series addressing the prevention of accidental releases of toxic chemicals. Phosgene, a highly reactive and corrosive liquid that boils at room temperature, has an Immediately Dangerous to Life and Health (IDLH) concentration of 2 ppm, which makes it a substantially acute toxic hazard. Reducing the risk associated with an accidental release of phosgene involves identifying some of the potential causes of accidental releases that apply to processes that use phosgene. The manual identifies examples of potential causes and measures that may be taken to reduce the accidental release risk. Such measures include recommendations on plant design practices, prevention, protection, and mitigation technologies, and operation and maintenance practices. Conceptual cost estimates of possible prevention, protection, and mitigation measures are provided.

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ABSTRACT

Recent headlines of accidental releases of toxic chemicals at Bhopal and Chernobyl have created the current public awareness of toxic release problems. As a result of other, perhaps less dramatic incidents in the past, portions of the chemical industry were aware of this problem long before these events. These same portions of the industry have made advances in this area. Interest in reducing the probability and consequences of accidental toxic chemical releases that might harm workers within a process facility and people in the surrounding community prompted the preparation of this manual and a planned series of companion manuals addressing accidental releases of toxic chemicals.

Phosgene is a highly reactive and corrosive liquid that boils at room temperature. It has an IDLH (Immediately Dangerous to Life and Health) concentration of 2 ppm, which makes it a substantial acute toxic hazard.

Reducing the risk associated with an accidental releases of phosgene involves identifying some of the potential causes of accidental releases that apply to the processes that use phosgene. In this manual examples of potential causes are identified as are specific measures that may be taken to reduce the accidental release risk. Such measures include recommendations on plant design practices, prevention, protection and mitigation technologies, and operation and maintenance practices. Conceptual cost estimates of possible prevention, protection, and mitigation measures are provided.

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SECTION 1

INTRODUCTION

1.1 BACKGROUND

Increasing concern about the potentially disastrous consequences of accidental releases of toxic chemicals resulted from the Bhopal, India, accident of December 3, 1984, which killed approximately 2,000 people and injured thousands more. A toxic cloud of methyl isocyanate was released. Concern about the safety of process facilities handling hazardous materials increased further after the accident at the Chernobyl nuclear power plant in the Soviet Union in April of 1986.

While headlines of these incidents have created the current awareness of toxic release problems, there have been other, perhaps less dramatic, incidents in the past. Interest in reducing the probability and consequences of accidental toxic chemical releases that might harm workers within a process facility and people in the surrounding community prompted the preparation of this manual and a series of companion manuals addressing accidental releases of toxic chemicals.

Historically, there has been a limited number of significant releases of phosgene both in the United States and abroad. In 1969 in LaPorte, Texas, an accidental release at a chemical plant injured two people. The release causing the greatest loss of life occurred in Hamburg, Germany, in 1928 when a phosgene storage tank failed. Ten people were killed (1).

1.2 PURPOSE OF THIS MANUAL

The purpose of this manual is to provide technical information about the prevention of accidental releases of phosgene. The manual addresses technological and procedural issues related to release prevention, associated with the storage, handling, and process operations involving phosgene as it is used in the United States. This manual does not address uses of phosgene not encountered in the United States.

This manual is intended as a summary manual for persons charged with reviewing and evaluating the potential for releases at facilities that use, store, handle, or manufacture phosgene. It is not intended as a specification manual, and in fact refers the reader to additional technical manuals and other information sources for more complete information on the topics discussed. Other information sources include manufacturers and distributors of phosgene, and technical literature on design, operation, and loss prevention in facilities handling toxic chemicals.

1.3 USES OF PHOSGENE

Commercial manufacture of phosgene is by the reaction of carbon monoxide with chlorine over a carbon catalyst. In the United States, approximately one million tons of phosgene were produced in 1986 by this process (2). As of 1985, 11 companies were manufacturing phosgene at 15 facilities, nationwide. Most of the phosgene produced is used captively at the production facility, although it is shipped in small cylinders (e.g., 150-pound) and one-ton containers.

The major use of phosgene in the United States is for the manufacture of isocyanates which consumes about 85 percent of the phosgene produced. Isocyanates are the precursors of polyurethane foam and rubber. Another 6 percent of the phosgene is used for the manufacture of polycarbonates.

A variety of goods including appliance and electrical tool housings, electronic parts, and break-resistant glazing are polycarbonate based. The remainder of the phosgene is used in the manufacture of specialty chemicals. These include herbicides, pesticides, dyes, pharmaceuticals, and others.

In the United States, phosgene is stored in small cylinders (e.g., 150-pound), one-ton containers, and bulk storage tanks.

1.4 ORGANIZATION OF THE MANUAL

Following this introductory section, the remainder of this manual presents technical information on specific hazards and categories of hazards for phosgene and their control. These are examples only and are representative of only some of the hazards that may be related to accidental releases.

Section 2 discusses physical, chemical and toxicological properties of phosgene. Section 3 describes the types of facilities which manufacture and use phosgene in the United States. Section 4 discusses process hazards associated with these facilities. Hazard prevention and control are discussed in Section 5. Costs of example storage and process facilities reflecting different levels of control are also presented in Section 5. The examples are for illustration only and do not necessarily represent a satisfactory alternative control option in all cases. Section 6 presents a reference list. Appendix A is a glossary of key technical terms that might not be familiar to all users of the manual, and Appendix B presents selected conversion factors between metric (SI) and English measurement units.

SECTION 2

CHEMICAL CHARACTERISTICS

This section of the manual describes the physical, chemical and toxicological properties of phosgene as they relate to accidental release hazards.

2.1 PHYSICAL PROPERTIES

Phosgene in the liquid phase, appears colorless turning slightly yellow in the presence of impurities. Gaseous phosgene, also colorless, is highly toxic and has been described as having an odor like musty hay (3) or decaying fruit (4). In dilute concentrations, phosgene odor has been compared to that of green corn (5). Selected physical properties of phosgene are listed in Table 2-1.

Phosgene exhibits only a slight solubility in water. Upon contact with water, phosgene slowly decomposes to hydrochloric acid and carbon dioxide. Phosgene reacts with alkali such as sodium hydroxide in water solution to form sodium chloride and sodium carbonate. Phosgene is soluble in aromatic and aliphatic hydrocarbons, chlorinated hydrocarbons, carbon tetrachloride, organic acids, and esters. Due to its high volatility, liquid phosgene will evaporate quickly when exposed to the air. In addition, phosgene possesses a vapor-phase density over three times that of air. Therefore, phosgene will tend to stay at ground level in the event of a release.

Liquid phosgene also has a large coefficient of thermal expansion. This can pose a special hazard for liquid-full equipment. A liquid-full vessel is a vessel that is not vented and is filled with liquid phosgene with little or no vapor space above the liquid. In these situations, there is no room for thermal expansion of the liquid, and temperature increases can result in containment failure.

TABLE 2-1. PHYSICAL PROPERTIES OF PHOSGENE

		Reference
CAS Registry Number	75-44-5	
Chemical Formula	$COCl_2$	
Molecular Weight	98.92	
Normal Boiling Point	45.5°F @ 14.7 psia	6
Melting Point	-198.1°F	6
Liquid Specific Gravity (H_2O=1)	1.387 @ 68°F	6
Vapor Specific Gravity (air=1)	3.4 @ 68°F	6
Vapor Pressure	23.4 psia @ 68°F	3
Vapor Pressure Equation		7

$$\log Pv = A - \frac{B}{T+C}$$

where: Pv = vapor pressure, mmHg
T = temperature, °C
A = 6.842, a constant
B = 941.25, a constant
C = 230.0, a constant

Solubility in Water	very slight with slow decomposition	8
Specific Heat at Constant Volume (Vapor)	0.119 Btu/lb-°F @ 59°F	8
Specific Heat at Constant Pressure (Vapor)	0.139 Btu/lb-°F @ 59°F	8
Specific Heat at Constant Pressure (Liquid)	0.116 Btu/lb-°F @ 43.3°F	8
Latent Heat of Vaporization	106.1 Btu/lb @ 45.5°F	3

(Continued)

TABLE 2-1 (Continued)

		Reference
Liquid Surface Tension	11.44 dynes/cm @ 68°F	3
Coefficient of Thermal Expansion @ 32°F	0.002207 per °F	8
Additional properties useful in determining other properties from physical property correlations:		
Critical Temperature	359.6°F	3
Critical Pressure	823.2 psia	3
Critical Density	32.46 lb/ft^3	3

2.2 CHEMICAL PROPERTIES AND REACTIVITY

Phosgene is not considered explosive or flammable. However, phosgene is highly reactive. The most significant chemical properties contributing to the potential for accidental release are as follows:

- Dry phosgene is stable at ordinary room temperature. At elevated temperatures, decomposition to chlorine and carbon monoxide occurs. This dissociation proceeds from 0.45 percent at 214°F to 100 percent at 1,472°F (8). Since one mole of phosgene decomposes to two moles of decomposition gases, pressures in containers would tend to increase dramatically at increasing temperatures. Therefore, exposure of phosgene containing equipment to excessive temperatures, such as from a fire, presents a high release hazard due to equipment failure.

- Phosgene reacts with many organic and inorganic compounds. Potentially violent reactions can occur, especially with aluminum (in the presence of moisture), isopropyl alcohol, potassium, sodium, tert-butyl azido formate, 2,4-hexadien-1,6-diol, hexafluoro-isopropylidene, amino lithium, and lithium (9).

- The hydrochloric acid formed when phosgene decomposes in the presence of water corrodes most common metals, which can lead to equipment failure.

- The introduction of water to a closed vessel containing phosgene can result in an increase in vessel pressure, in addition to corrosion, since for every mole of phosgene reacting with water, three moles of gases are formed (two moles of HCl and one mole of CO_2). This pressure increase can cause containment failure, especially when corrosion occurs.

2.3 TOXICOLOGICAL AND HEALTH EFFECTS

Phosgene is a highly toxic gas by inhalation and is irritating to the eyes and skin. Phosgene hydrolyzes to hydrochloric acid in the respiratory system. Victims exposed to phosgene gas may not develop serious symptoms for several hours. For victims receiving even a fatal dose, immediate symptoms may be relatively mild. After a latent period, however, burning in the throat and chest, shortness of breath, labored breathing and coughing of bloody sputum are common symptoms. In fatal cases, pulmonary edema leads to death by asphyxiation; in non-fatal cases, weakness which may last for months.

Table 2-2 presents a summary of some of the exposure limits of phosgene. Table 2-3 presents a summary of predicted human health effects of exposure to various concentrations of phosgene.

TABLE 2-2. EXPOSURE LIMITS FOR PHOSGENE

	Concentration (ppm)	Description	Reference
PEL	0.1	A time-weighted 8-hour exposure to this concentration, as set by the Occupational Safety and Health Administration (OSHA), should result in no adverse effects for the average healthy male worker.	10
IDLH	2	The concentration defined as posing an immediate danger to life and health (i.e., causes irreversible toxic effects for a 30-minute exposure).	11
TC_{LO}	25	This concentration is the lowest published concentration causing toxic effects (irritation) for a 30-minute exposure.	12
LC_{LO}	82	This concentration is the lowest published lethal concentration for a human over a 30-minute exposure.	12

TABLE 2-3. PREDICTED HUMAN HEALTH EFFECTS OF EXPOSURE TO VARIOUS CONCENTRATIONS OF PHOSGENE

Concentration ppm	Predicted Effect	Reference
3.1	Minimum concentration known to cause throat irritation.	3
4.0	Minimum concentration known to cause eye irritation.	3
4.8	Minimum concentration known to cause coughing.	3
5.6	Odor threshold.	3
25	Dangerous for exposure of 30-60 minutes.	3
120	Lethal within 10 minutes.	3
167	Lung injury in 2 minutes.	3
400	Likely fatal in 2 minutes.	8

SECTION 3

FACILITY DESCRIPTIONS

This section briefly describes the manufacture and uses of phosgene in the United States. Major hazards of these processes associated with accidental releases are discussed in Section 4. Preventive measures associated with these hazards are discussed in Section 5.

3.1 PHOSGENE MANUFACTURE

Phosgene is manufactured by the gas phase reaction of carbon monoxide and chlorine over an activated carbon catalyst. A flow diagram of the phosgene manufacturing process is presented in Figure 3-1.

The reaction is carried out at a temperature of approximately 390°F and at a pressure ranging from 2 to 4 psig (13). The reaction is rapid and highly exothermic, with a heat of reaction of 47,500 Btu/lb-mole (7). To aid heat transfer, the reactor is designed with 2 inch carbon-filled tubes which are water-cooled (13).

The reaction proceeds by pre-mixing carbon monoxide and chlorine with a small excess of carbon monoxide to ensure complete utilization of chlorine. Approximately 99 percent conversion to phosgene occurs. After exiting the reactor, the phosgene product is typically distilled, condensed and sent to storage. If high purity phosgene is not required, the reaction gases may simply be condensed, eliminating the distillation step. The remaining non-condensible gases are sent to tail gas scrubbers and an incinerator or flare to remove or destroy residual phosgene.

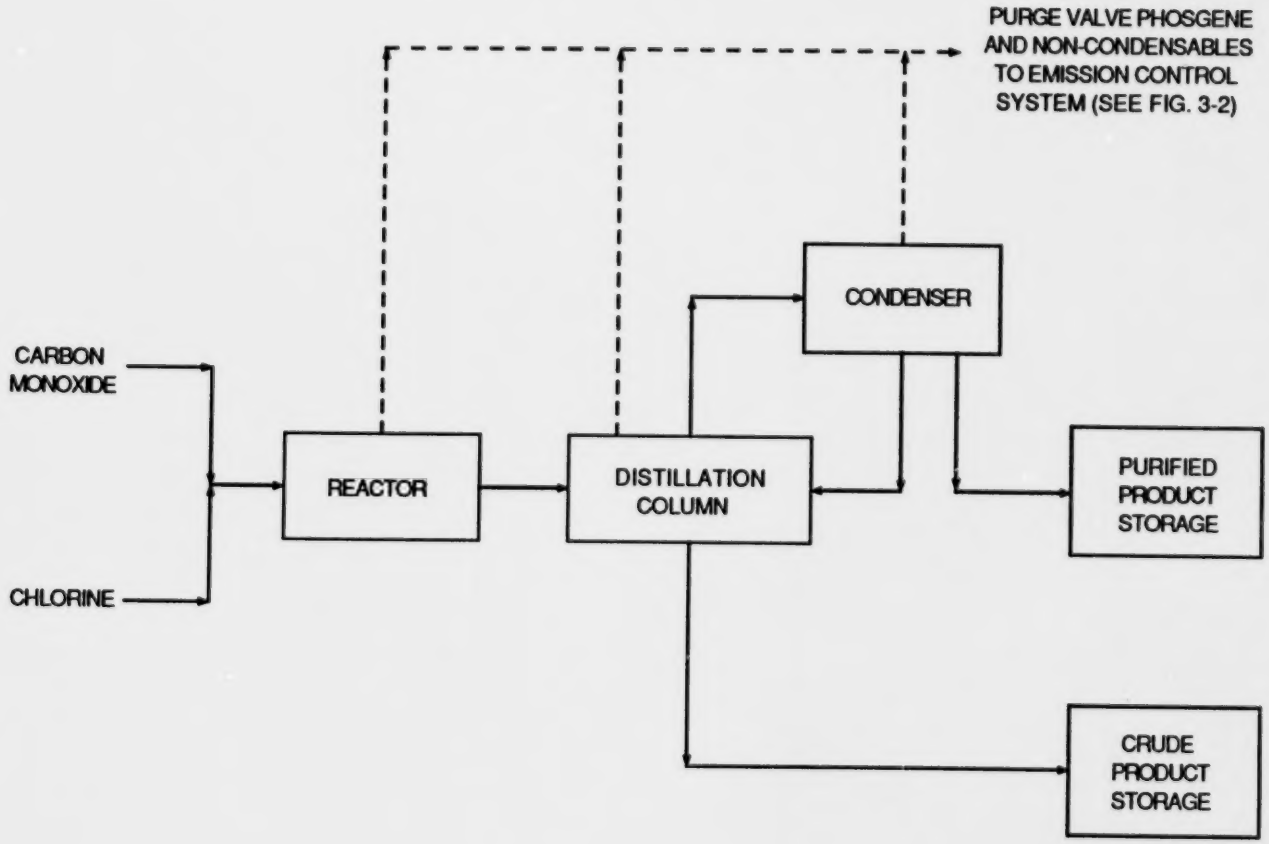


Figure 3-1. Conceptual diagram of a typical phosgene manufacturing process

Source: Adapted from Reference 14.

Process emissions are routed to an emission control system as shown in Figure 3-2. Typically, the phosgene-laden gas enters a water scrubber, followed by a caustic scrubber, incinerator, and a second caustic scrubber. The upstream caustic scrubber incorporates an aqueous sodium hydroxide solution which effectively destroys phosgene by forming sodium chloride and sodium carbonate. Phosgene exhibits a low solubility in the caustic solution. As a result, the scrubber can accommodate a limited phosgene loading in the emission gas. As depicted in Figure 3-2, a water scrubber is often placed upstream of the caustic scrubber. Phosgene hydrolyzes in water, producing hydrochloric acid and carbon monoxide. The water scrubber also recovers any hydrochloric acid present in the process emission gas. After exiting the caustic scrubber, the emission gases are incinerated. The downstream caustic scrubber removes acid gases formed by the combustion of chlorinated hydrocarbons.

High hazard areas in the manufacturing process of phosgene include the following:

- Reactor feed system;
- Phosgene reactor;
- Distillation column; and
- Phosgene condenser.

Carbon monoxide and chlorine used in the manufacture of phosgene must be free of water to prevent hydrochloric acid formation and corrosion. Small amounts of moisture in the system may result in a protracted and undetected corrosion problem leading eventually to an unexpected equipment failure. Also, wet phosgene readily decomposes to hydrochloric acid and carbon dioxide in the presence of water. In closed vessels, a pressure buildup will occur since three moles of gas are produced for every mole of phosgene reacted with water. Containment failure and a direct release of phosgene may result. In addition, contamination of the carbon monoxide feed with methane or hydrogen can lead to a runaway reaction when carbon monoxide is mixed with chlorine in the feed line to the reactor (13,15).

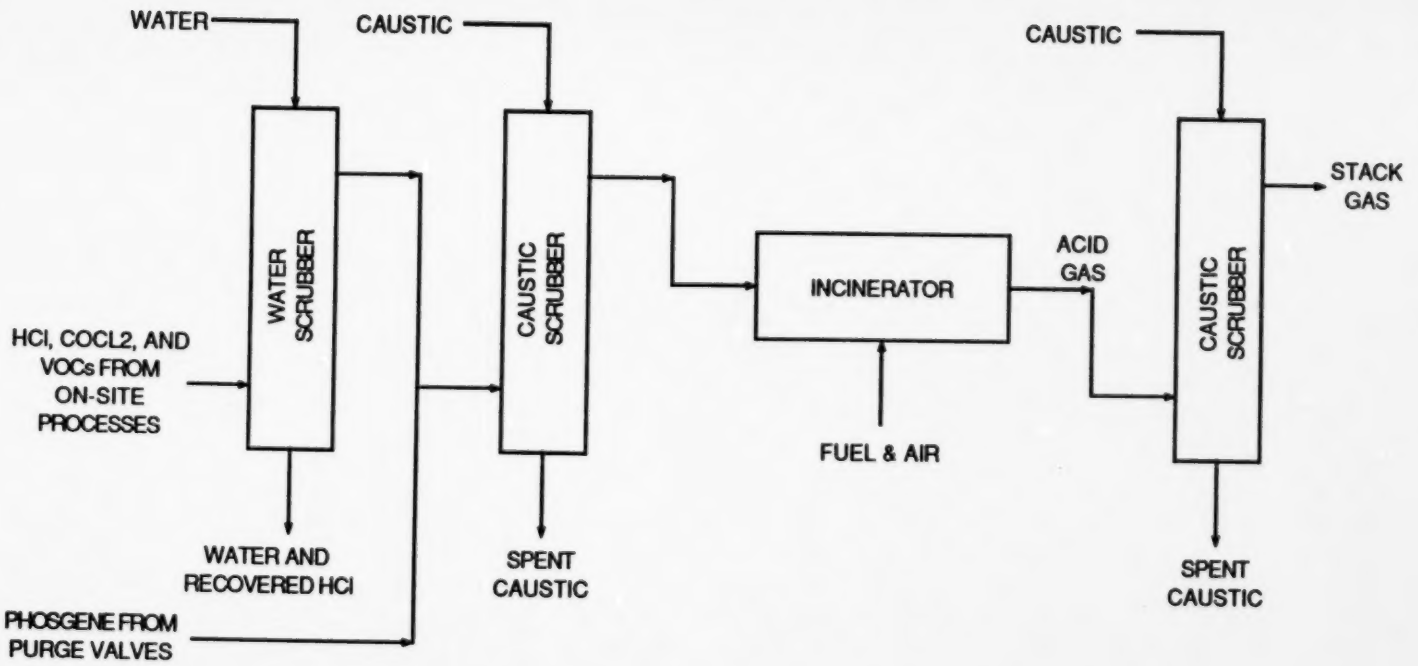


Figure 3-2. Conceptual diagram of phosgene emission control system used with typical phosgene manufacturing process.

Source: Adapted from Reference 13.

Failure of the reactor cooling system to sufficiently remove the heat generated during the reaction will cause hot spots to develop in the reactor. The resulting temperature rise can result in decomposition of phosgene into the starting materials and a pressure buildup and potential overpressure of the reactor. Likewise, the use of water-cooled reaction tubes also presents the possibility of a leak of phosgene into the cooling water system leading to hydrochloric acid formation and potential failure of these tubes due to corrosion.

Excessively high chlorine and carbon monoxide feed rates could result in overpressurization of the reactor or cause uncontrolled surges of chlorine, carbon monoxide, or phosgene to pass through the reactor to downstream processing where it might cause a process upset leading to overpressure or emergency venting. In addition, excessive feed rates could lead to a runaway reaction as a result of the large exotherm produced during the reaction.

The phosgene distillation and condenser units are subject to overpressure and/or overheating. The reboiler and bottoms pumps are potential weak points since operating conditions are severe. Loss of cooling in the condenser could cause overpressure. This could result from insufficient cooling water, a complete loss of cooling water, or undetected leakage of phosgene into the cooling system contributing to protracted corrosion and ultimately equipment failure.

3.2 PHOSGENE CONSUMPTION

The major uses for phosgene in the United States are isocyanate and polycarbonate manufacture. Phosgene is also used in the manufacture of various herbicides, pesticides, dyes, and pharmaceuticals. Table 3-1 presents a listing of some of the products that might be manufactured using phosgene.

This subsection summarizes some of the major technical features, related to release hazards, of typical phosgene processing facilities that might be found in the United States.

TABLE 3-1. TYPICAL USES OF PHOSGENE

Organic Carbonates
- diethyl carbonate
- dimethyl carbonate
- ethylene carbonate
- dipropyl carbonate
- diallyl carbonate
- diphenyl carbonate

Organic Chloroformates
- methyl chloroformate
- isopropyl chloroformate
- benzyl chloroformate
- ethyl chloroformate
- 2-ethylhexyl chloroformate
- isobutyl chloroformate
- sec-butyl chloroformate
- n-propyl chloroformate
- allyl chloroformate
- n-butyl chloroformate
- decyl chloroformate
- phenyl chloroformate

Isocyanates
- toluene diisocyanate
- diphenyl-methane-4,4'-diisocyanate
- other monoisocyanates and polyisocyanates

Polycarbonates

Herbicides and Pesticides
- phenyl ureas
- carbonates
- thiocarbonates

Chlorocarbonates

Urethanes

Thiochloroformates

Carbamoyl Chlorides

Pyrocarbonates

Carbazates

Carbohydiazides

Malonates

Carbodiimides

Oxazolidinediones

Source: References 3, 8, 13, 14, 16.

3.2.1 Isocyanate Manufacture

Isocyanate manufacture is the largest use of phosgene in the United States. Isocyanates can be divided into two major groups: aromatic and aliphatic isocyanates. Aromatic isocyanates are more important commercially than aliphatic isocyanates (13).

Aromatic Diisocyanate Manufacture--

Of the aromatic isocyanates manufactured using phosgene, toluene diisocyanate (TDI) and diphenyl-methane-4,4'-diisocyanate (MDI) are the most prevalent. Figure 3-3 illustrates a typical process for the manufacture of toluene diisocyanate.

A solution of diamino-toluene in an organic solvent is fed to the primary reaction vessel. A solution of phosgene in the same solvent is also fed to the reactor. The choice of solvent has been found to affect the rate and extent of the phosgenation reaction (16). Xylene, monochlorobenzene, or o-dichlorobenzene are commonly used. The reaction is endothermic and occurs at temperatures below 140°F. The solution is then fed to a second and possibly third reaction vessel, operating at increasing temperatures of up to approximately 400°F. Each vessel receives a fresh supply of phosgene or phosgene in solution. The entire reaction process requires a residence time of several hours (16).

After completion of the reaction, the solution reaches the fractionating columns where the isocyanate product, solvent, hydrochloric acid, excess phosgene, and distillation residuals are separated. The solvent stream is recycled for reuse. The hydrochloric acid vapors and unreacted phosgene may be recovered for further use or disposed of by scrubbing, depending on the specific facility. The hydrochloric acid can be sold or decomposed to hydrogen (for nitro compound hydrogenation) and chlorine for phosgene synthesis or sold. Residuals from the fractionator bottoms are incinerated.

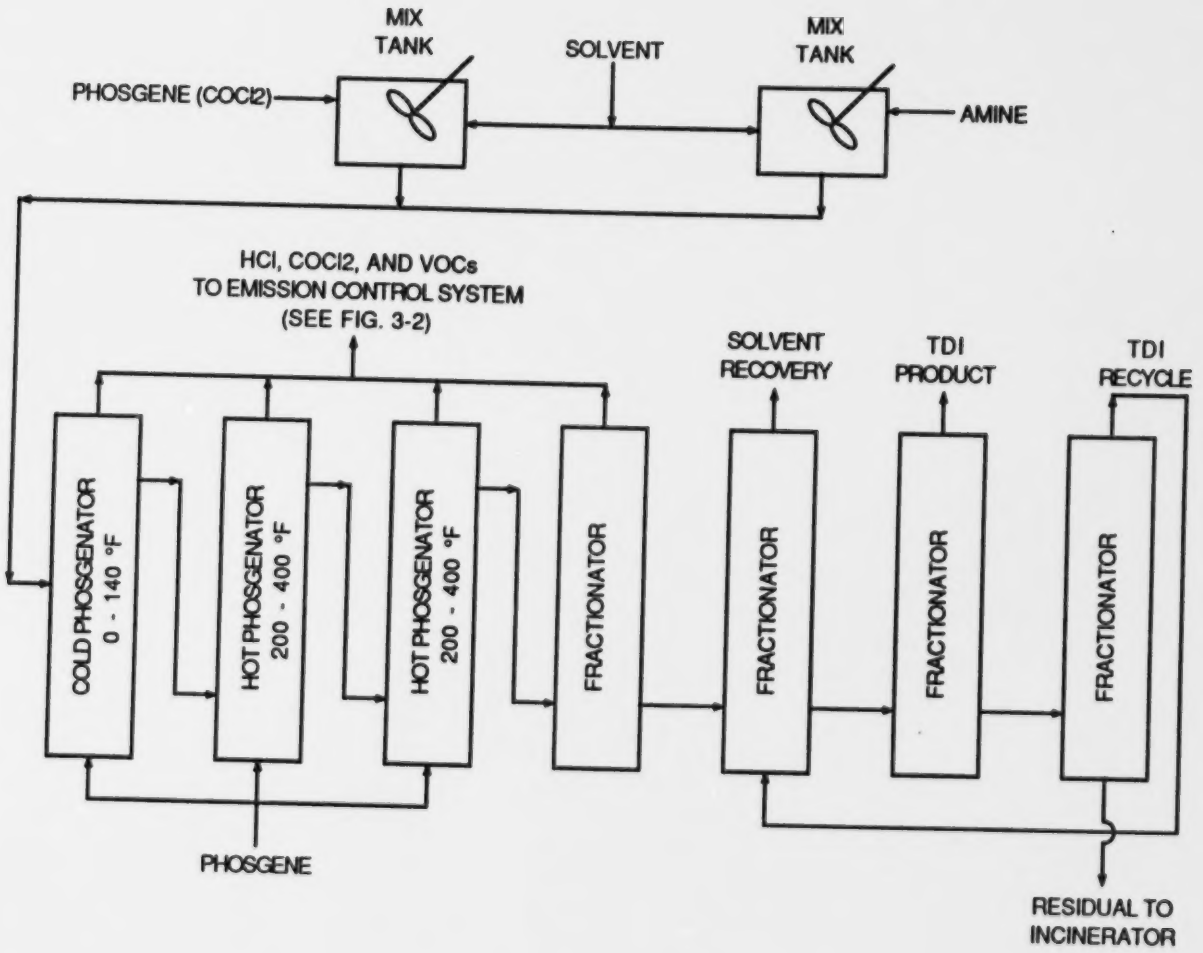


Figure 3-3. Conceptual diagram of a typical manufacturing process for toluene diisocyanate.

Source: Adapted from References 16 and 17.

All process emissions are sent to an emission control system similar to the one used by the phosgene manufacturing process (see Figure 3-2).

High hazard areas in the manufacture of TDI include the following:

- Mix tank feed stream;
- Reaction vessels; and
- Fractionation columns.

The amine and solvent feeds must be free of water. Water reacts exothermically with phosgene and TDI, producing carbon dioxide and hydrochloric acid. The resulting temperature and pressure rise and the corrosive acid can lead to a system failure. Excess phosgene feed to the mix tank can result in overpressure of the mix tank or allow unreacted phosgene vapor to pass through the reactor to downstream processing where it might cause a process upset leading to overpressure or emergency venting.

In the reactors, operating temperatures must be closely monitored, keeping them below predetermined values which are a function of the extent of diamine-toluene conversion. If heated indiscriminately, the decomposition of diamine-toluene can result in a pressure increase in the reactor and possible containment failure. A loss of temperature control could also cause excess phosgene vapor to be released resulting in potential overpressure. A leak of phosgene into the reactor cooling system could result in protracted corrosion and potential equipment failure.

The fractionating columns are subject to potential overheating and overpressure since these operations have a thermal energy input. Additional hazards are similar to those described for the reaction vessels.

Manufacture of the other major phosgene-based aromatic diisocyanate, diphenyl-methane-4,4'-diisocyanate (MDI), occurs under reaction and process conditions similar to those used in the manufacture of TDI. However, the feedstock incorporates methylenedianiline (MDA) and polymeric MDA.

The process consists of the phosgenation of MDA followed by the polymerization of the resulting diisocyanate product. Both reactions are carried out in a solvent medium. The solvent dissolves the amine, phosgene, isocyanate monomers, and the lower weight polymers. The solvent, hydrogen chloride formed during the reactions, and unreacted phosgene are recovered from the process in a manner similar to that used in the TDI process.

The product MDI must be quench-cooled to prevent the dimer content from exceeding approximately one percent (16). Slow cooling can result in a dimer content which exceeds the solubility in the isocyanate mixture. This could lead to equipment plugging and attendant operational problems

Aliphatic Isocyanate Manufacture--

Aliphatic isocyanate manufacture involves the same general process and process conditions as the aromatic isocyanates. The feedstocks and reaction stoichiometry are different. Also, to stabilize the amine groups, formation of a salt prior to phosgenation is often required (18).

3.2.2 Polycarbonate Manufacture

Polycarbonate manufacture involves the reaction of a diol (an alcohol with two alcohol functional groups in the molecule) and phosgene. The resulting reaction produces the polycarbonate and hydrochloric acid.

Most polycarbonates are derived from the reaction of bisphenol-A [2,2-bis-(4-hydroxyphenyl)-propane] and phosgene. Figure 3-4 illustrates a typical manufacturing process. In this process, bisphenol-A and a trace amount of a monofunctional phenol are dissolved in an aqueous sodium hydroxide slurry. A solvent such as methylene chloride and a tertiary amine catalyst, such as pyridine are introduced into the reactor. Phosgene gas is bubbled through a continuously mixed slurry. Additional caustic is added to keep the solution basic. After completion of the reaction, the organic and aqueous phases are separated. The organic phase contains methylene chloride, residual

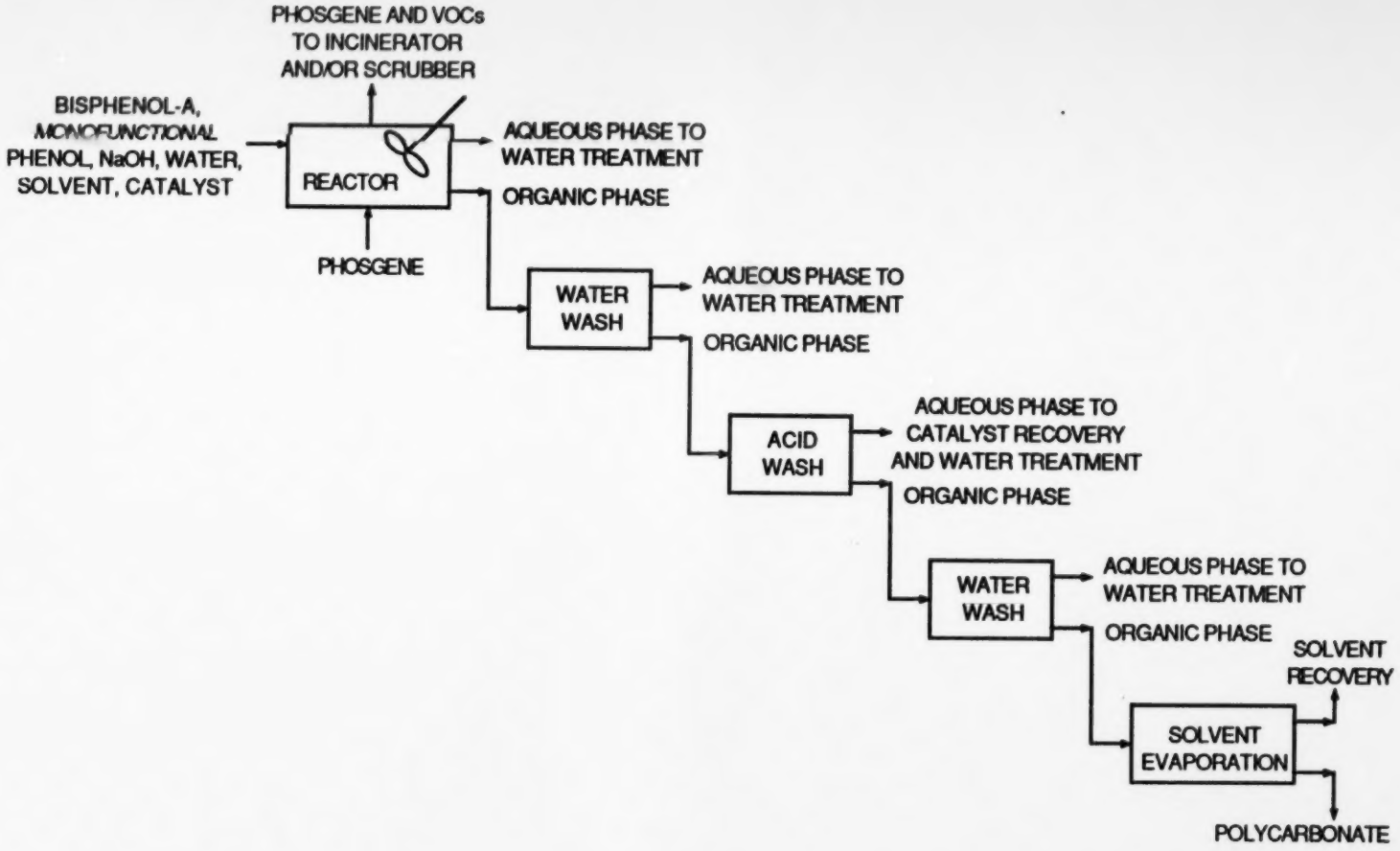


Figure 3-4. Conceptual diagram of a typical manufacturing process for polycarbonate.

Source: Adapted from Reference 16.

catalyst, and the polycarbonate product. This solution is washed with water, extracted with acid to remove catalyst residues, and repeatedly washed with water until neutral. The methylene chloride is then evaporated from the organic solution, leaving the polycarbonate product.

Parts of the process that are of concern when considering a phosgene release are the phosgene feed system, the reaction vessel and the incinerator. Of significant importance is the fact that phosgene readily decomposes when bubbled through the caustic slurry. The pH of the slurry must be kept strongly alkaline to prevent the phosgene from hydrolyzing to hydrochloric acid and carbon dioxide and causing equipment corrosion.

The temperature and pressure of the reactor must be closely monitored. At the onset of the reaction, elevated pressure is required to prevent foaming of the methylene chloride/polymer solution and maintain the polymer above its solidification point. Foaming complicates heat and mass transfer and can lead to solidification of the polymer and plugged equipment since the polymer has a high solidification temperature. Without proper mixing, the reactor temperature will increase further and decomposition of phosgene will occur. The resulting pressure buildup may lead to overpressure and a direct release of phosgene.

An excessively high phosgene feed rate could result in overpressuring the reactor or cause unreacted phosgene to pass through the reactor to downstream processing where it might cause a process upset leading to overpressure or emergency venting. Likewise, a loss of bisphenol-A flow could result in incomplete reaction of phosgene leading to overpressure. A liquid level below the phosgene introduction point could also cause a phosgene release due to overpressure. If the incinerator and/or caustic scrubber on the reactor vent stream are not sized for the excess phosgene, a direct release of phosgene could occur.

3.2.3 Herbicides and Pesticides Manufacture

Phosgene is an intermediate in the synthesis of numerous herbicides and pesticides. The phosgene molecule reacts with an amine group ($-NH_2$) to yield hydrochloric acid and a substituted isocyanate group (-N=C=O). Three general classes of herbicides and pesticides employing phosgene are phenyl ureas, carbamates, and thiocarbamates. Each of these classes is discussed in the following subsections.

Substituted Phenyl Ureas--

There are currently 20 to 25 phenyl ureas commercially produced (13). Figure 3-5 represents a generalized flow diagram for the manufacture of phenyl ureas. The manufacture of 3-para-chlorophenyl-1,1-dimethyl urea (monuron) is one example of a typical reaction process. In this process, para-chloroaniline in an inert solvent reacts with phosgene and anhydrous hydrogen chloride at 160 to 170°F to form para-chlorophenyl isocyanate (13). The para-chlorophenyl isocyanate reacts further with dimethyl amine at 77°F to yield monuron (13). The ureas are generally insoluble in the inert solvents and are separated by precipitation and evaporation.

Carbamates--

Carbamates, used as herbicides, insecticides, and pharmaceuticals, are synthesized by either the reaction of a substituted aniline with a chloroformate ester, or the reaction of an isocyanate with an alcohol.

The formation of the chloroformate ester requires the reaction of phosgene with an alcohol. Isocyanate formation employs the reaction of phosgene with an amine. Carbamate manufacture follows the generalized flow diagram of Figure 3-5 (13).

Thiocarbamates--

Thiocarbamates are used primarily as herbicides, but some have shown to possess fungicidal activity as well (16). The formation of thiocarbamates is

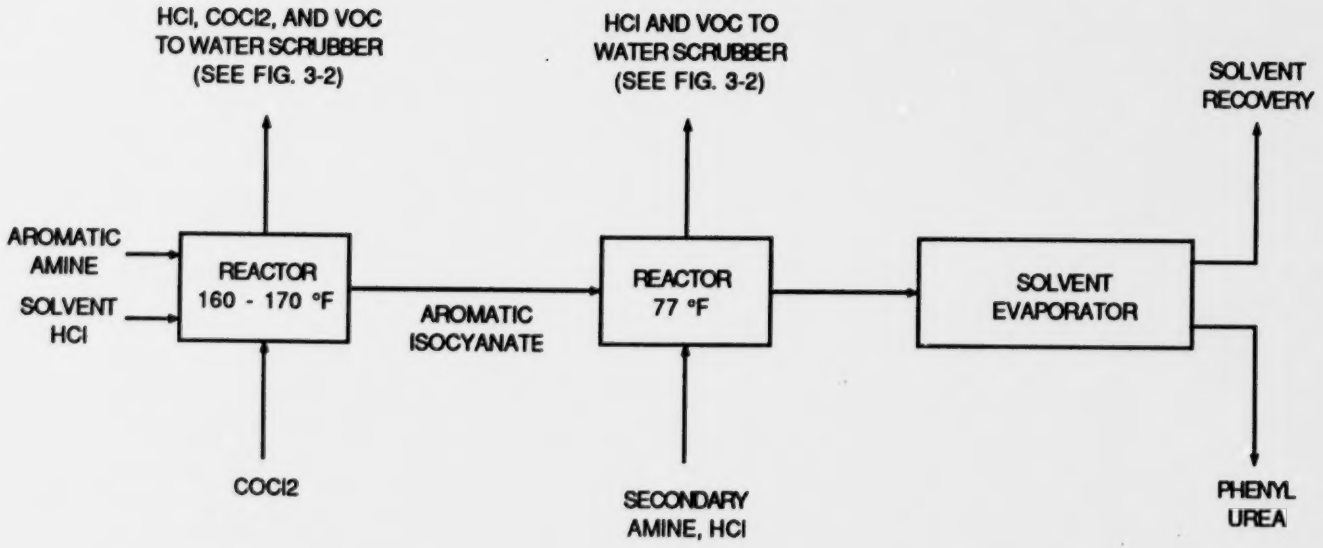


Figure 3-5. Conceptual diagram of a typical manufacturing process for phenyl ureas.

Source: Adapted from Reference 13.

a two-stage process. The first stage involves the reaction of phosgene and a secondary amine to yield a carbamyl chloride. The carbamyl chloride subsequently reacts with a thiol to yield the thiocarbamate. This synthesis employs the same general process configuration as the other herbicides and pesticides previously discussed in this section.

High hazard areas in these processes include the following:

- Phosgene feed rate system;
- Reactor cooling system;
- Composition of feed streams; and
- Phosgene scrubber.

An excessively high phosgene feed rate or a loss of reactant flow with incomplete reaction could result in overpressuring the reactor or cause unreacted phosgene to pass through the reactor to downstream processing where it might cause a process upset leading to overpressure or emergency venting.

Operating conditions of the reactors must be closely monitored to maintain a low temperature and avoid decomposition of phosgene. This decomposition could lead to a pressure increase and potential containment failure.

The feed streams to the reactors must be kept water-free. If water does enter a reaction vessel, it can combine with the anhydrous hydrogen chloride feed in the phenyl urea process to form highly corrosive hydrochloric acid and lead to eventual equipment failure. In addition, hydrolysis of wet phosgene can occur in all process units resulting in a hazardous increase in pressure.

Finally, failure of the scrubber on the vent stream of a reactor could lead to a direct release of phosgene. Also, in the event of an excess phosgene feed rate, inadequate sizing of the scrubber could also result in equipment failure and/or a direct release of phosgene.

3.2.4 Other Chemicals

A variety of other chemicals are manufactured using phosgene as was shown in Table 3-1. Although each individual chemical is different, their manufacturing processes are in many ways similar to those presented previously in this section. Likewise, the hazards associated with their manufacture will also be similar. In general, the primary hazards are those associated with the feed stream flow rates and compositions, overheating, and overpressure.

Since many of the chemicals involve exothermic reactions, proper cooling is required to maintain reactor control. A loss of cooling can lead to a runaway reaction and overpressure. Feeds must be free of contaminants (e.g., water) to prevent undesired reactions and corrosion due to the hydrolysis of phosgene. The hydrolysis of phosgene can also lead to a pressure increase in vessels by the formation of carbon dioxide and hydrogen chloride gases. Since all of the chemicals require the addition of phosgene either in solution or as a gas, loss of feed control can result in a buildup of excess phosgene and potential overpressure in either the reactor or in downstream process units.

Additional hazards must be determined on a case-by-case basis. More detailed discussion of process hazards and their controls can be found in the user's guide and a manual on control technologies in the prevention reference manual series of which this manual is a part (19,20).

3.3 STORAGE AND HANDLING

Phosgene producers and users are currently reducing storage of phosgene (21). With many users, the phosgene is produced on site for captive use. Of the phosgene still being stored, pressurized carbon-steel storage vessels are used. Instead of using a single large vessel, phosgene is commonly stored in several smaller vessels (22). This reduces the quantity of phosgene potentially released from a single vessel failure. Another common practice is to store the material in two tanks, each tank only half full (13). In the case of a leak, the phosgene can be transferred to the secure vessel.

The storage vessels are fitted with a number of safety features. Excess flow devices are often installed on the vessel discharge lines. The excess flow devices shut off flow through the line in which they are installed if a line rupture or leak occurs downstream. Dikes are constructed around the vessels. Also, deluge systems are incorporated into the storage vessel design. Upon rupture of the vessel, an alkali solution, sodium hydroxide, for example, is sprayed from above the storage vessel. The alkali solution reacts with the phosgene to form a solution of sodium chloride and carbonate. Finally, pressure relief devices are routed to a caustic scrubber or flare.

Most of the phosgene manufactured in the United States is for captive use at the production facility. In fact, less than 1 percent of all phosgene manufactured in the Untied States is sold commercially. Of that sold, strict limitations on the transportation of phosgene have been enacted by the Department of Transportation (23). Two vessels have been approved for transporting phosgene: 150-pound cylinders and one-ton containers.

The 150-pound cylinders are constructed of steel. The cylinder valve assembly contains both liquid and gas ports. Both ports are 1/8" standard pipe size female openings normally fitted with brass or steel pipe plugs. From the liquid port, a 1/8" steel dip pipe extends into the cylinder to within 3/4" from the bottom. The gas port terminates immediately below the base of the valve body. Adjacent to each port is a valve to control flow. The valves are located counterclockwise from their respective outlet ports as viewed from above. The cylinders are fitted with an extension sleeve or skirt to protect the valve assembly.

The one-ton containers are also constructed of steel. Figure 3-6 illustrates a one-ton phosgene container. An eductor pipe extends internally from each valve to the nearest side of the tank. Therefore, either valve will emit liquid or gas depending on the position of the cylinder. With the two valve stems in a vertical line, the upper valve will generally emit gas, the

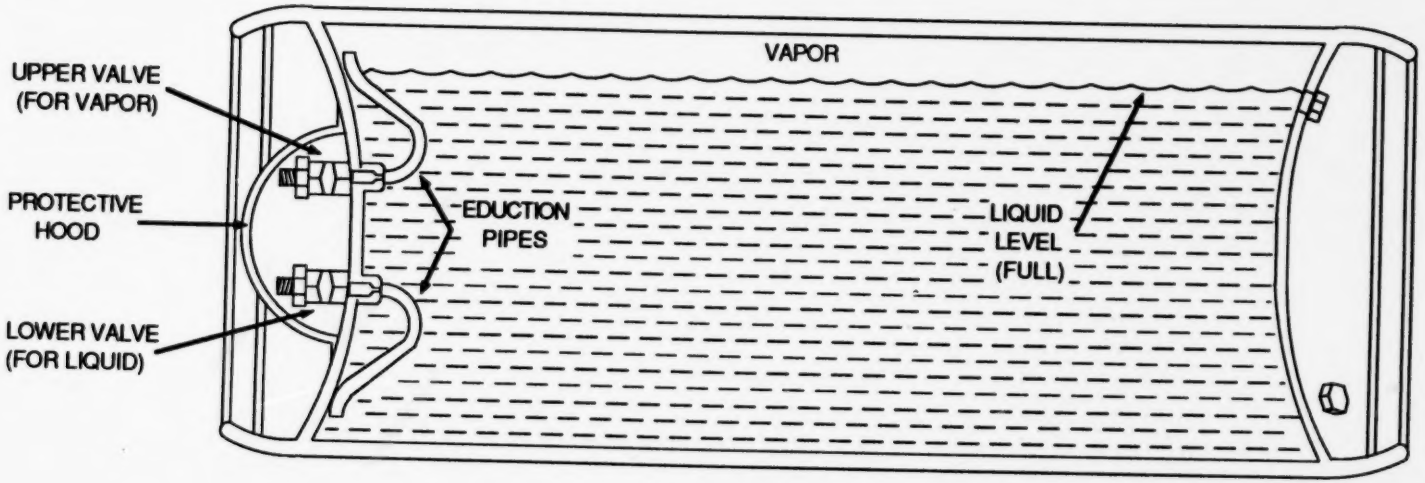


Figure 3-6. Conceptual diagram of typical one-ton phosgene container.

Source: Adapted from Reference 14.

lower valve liquid. To prevent leakage, the valves are fitted with a screwed cap and gasket. Concave ends of the tank protect the valve assembly. To further protect the valve assembly and prevent leakage, the valve assembly is fitted with a flanged bonnet bolted to a pad seal.

No pressure relief devices are permitted on either the 150-pound cylinders or one-ton containers.

For either the storage or transportation of phosgene, several hazards of accidental releases are present:

- Moisture entering the storage vessel can cause corrosion of the carbon steel, a commonly used material of construction for storage of phosgene, which can lead to equipment failure. Also, increased pressure by the formation of carbon dioxide and hydrogen chloride could contribute to equipment failure.

- Cylinder and ton container temperatures must be maintained below 125°F (8). Temperatures in excess of 125°F may cause the vessel to become liquid full resulting in dangerous hydrostatic pressures and a potential rupture since pressure safety relief devices are not permitted on these vessels.

- Overfilling of storage vessels may occur as a result of a malfunctioning scale, level gaging device, or operator error.

- Where phosgene is stored as a refrigerated liquid, a loss of refrigeration can result in overpressure and potential vessel failure.

- Errors in loading and unloading procedures such as loose connections or failure to close a valve when connecting or disconnecting lines.

SECTION 4

PROCESS HAZARDS

Some of the specific process hazards associated with the manufacture and uses of phosgene were cited in the previous section of this manual. This section presents some examples of more general causes of releases which may be common to any phosgene process.

Phosgene releases can originate from many sources including ruptures in process equipment, separated flanges, actuated relief valves or rupture discs, and failed pumps or compressors. In addition, losses may occur through leaks at joints and connections such as flanges, valves, and fittings where failure of gaskets or packing might occur.

Properties of phosgene which can promote equipment failure are its reactivity and its high liquid coefficient of thermal expansion. Reactivity manifested in corrosion is a likely general cause of equipment failure. Evaporators and metering and control equipment are especially sensitive if they are in intermittent use where moisture might enter the system.

Liquid or vapor phosgene releases may occur. Liquid spills can occur when phosgene is at or below its boiling point of 45.5°F, or when a sudden release of phosgene at temperatures above 45.5°F results in evaporative cooling of the remaining liquid by vapor flashing. Direct releases of vapor can also occur from the vapor spaces of containers or lines containing the vapor.

4.1 POTENTIAL CAUSES OF RELEASES

Failures leading to accidental releases may be broadly classified as due to process, equipment, or operational causes. This classification is for convenience only. Causes discussed below are examples only and do not necessarily include all possibilities. A more detailed discussion of possible causes of accidental releases is presented in a companion manual on control technologies in the prevention reference manual series of which this present manual is a part (20).

4.1.1 Process Causes

Process causes are related to the fundamentals of process chemistry, control, and general operation. Examples of process causes of a phosgene release include:

- Overpressure of any storage or process vessel containing phosgene due to decomposition of phosgene to hydrogen chloride and carbon dioxide from contamination with water;

- Overpressure of any storage or process vessel containing phosgene due to contamination with phosgene reactive materials;

- Overpressure of any storage or process vessel containing phosgene due to excess temperature resulting in decomposition;

- Excess phosgene feed leading to overfilling or overpressuring equipment;

- Loss of reactant feed leading to incomplete reaction and a buildup of excess phosgene leading to overpressure;

- A liquid level below the phosgene introduction point to a reactor causing an accumulation of unreacted phosgene vapor and potential overpressure;

- Loss of agitation in batch reactor systems leading to accumulation of unreacted phosgene or loss of cooling effectiveness;

- Loss of cooling or temperature control of reactor system resulting in a runaway exothermic reaction or thermal decomposition;

- Loss of condenser cooling in distillation units;

- Loss of pH control in caustic slurry reactors resulting in the decomposition of phosgene to carbon dioxide and hydrochloric acid. Such decomposition could result in overpressure;

- Contamination of feed streams with water leading to potential corrosion and eventual equipment failure;

- Backflow of process reactants to a phosgene storage vessel; and

- Contamination of carbon monoxide feed to phosgene reactor with methane or hydrogen leading to runaway reaction when mixed with chlorine feed.

4.1.2 Equipment Causes

Equipment causes of accidental releases result from hardware failure. Some possible causes include:

- Failure of vessels at normal operating conditions due to weakening of equipment from excessive stress or corrosion; excessive stress can be caused by improper fabrication, construction, installation, or external loading;

- Mechanical fatigue and shock in any equipment. Mechanical fatigue could result from age, vibration, or stress cycling, caused by pressure cycling, for example. Shock could occur from collisions with moving equipment such as cranes or other equipment in process or storage areas;

- Creep failure in equipment subjected to extreme operational upsets, especially excess temperature. This can occur in equipment subjected to fire that may have caused damage before being brought under control;

- Failure of any equipment that is exposed to phosgene due to stress corrosion cracking, especially equipment subject to vibration or other forms of mechanical stress; and

- All forms of corrosion; specific type will be process and material specific.

4.1.3 Operational Causes

Operational causes of accidental releases are a result of incorrect operating and maintenance procedures or human errors (i.e., not following correct procedures). These causes include:

- Overfilled storage vessels due to a lack of attention, failure to shutoff a flow or failure to note a partially full vessel before adding more material;

- Errors in loading and unloading procedures such as failure to make proper connections and failure to close a valve when disconnecting a hose line;

- Inadequate maintenance in general, but especially on pressure relief systems and other preventive and protective systems;

- Lack of inspection and non-destructive testing of vessels and piping to detect corrosion weakening; and

- Incomplete knowledge of the properties of a specific chemical system or process leading to unexpected corrosion or chemical reactions that could cause excessive heat or pressure.

SECTION 5

HAZARD PREVENTION AND CONTROL

5.1 BACKGROUND

Prevention of accidental releases relies on a combination of technological, administrative, and operational practices. These practices apply to the design, construction, and operation of facilities where phosgene is stored and used. Considerations in these areas can be grouped as follows:

- Process design;
- Physical plant design;
- Operating and maintenance practices; and
- Protective systems.

In each of these areas, consideration must be given to specific factors that could lead to a process upset or failure which could directly cause a release of phosgene to the environment, or result in an equipment failure which would cause the release. At a minimum, equipment and procedures should be in accordance with applicable codes, standards, and regulations. In addition, stricter equipment and procedural specifications should be in place if extra protection against a release is considered appropriate (e.g., as determined by a hazard assessment).

The following subsections discuss some specific aspects of the above areas as they relate to release prevention. In addition, illustrative cost estimates for different levels of control applied to storage and process facilities are also included. More detailed discussions can be found in the manual on control technologies, part of this prevention reference manual series (20).

5.2 PROCESS DESIGN

Process design involves the fundamental characteristics of the processes which use phosgene. This includes an evaluation of how deviations from intended process design features might initiate a series of events that could result in an accidental release. The primary focus is on how the process is controlled in terms of the basic process chemistry, and the variables of flow, pressure, temperature, composition, and level. Additional process design issues may include quantity measuring systems, mixing systems, fire protection, and process control instrumentation. Modifications to enhance process integrity may result from a review of these factors and could involve changes in quantities of materials, process pressure and temperature conditions, the unit operations, the sequence of operations, the process control strategies, and the instrumentation used.

Table 5-1 shows the relationship between some key process design considerations and individual processes described in Section 3 of this manual. This does not mean that other factors should be ignored, nor does it mean that proper attention to the key considerations ensures a safe system. However, the items listed, and perhaps others, must be properly addressed if a system is to be safe.

5.3 PHYSICAL PLANT DESIGN

Physical plant design considerations include equipment, siting and layout, and transfer/transport facilities. Vessels, piping and valves, process machinery, instrumentation, and factors such as location of systems and equipment must all be considered. The following subsections cover various aspects of physical plant design beginning with a discussion of materials of construction. This section is not intended to provide detailed specifications for the design of a facility handling phosgene. The discussion is intended to

TABLE 5-1. EXAMPLES OF KEY PROCESS DESIGN CONSIDERATIONS FOR PHOSGENE PROCESSES

Process Design Consideration	Process or Unit Operation
Contamination (water)	All
Contamination (methane, hydrogen)	Phosgene manufacture
Flow control of phosgene feeds	All
Temperature monitoring; heating media flow control	Phosgenation reactors
Adequate pressure relief	All
Mixing	All continuous stirred tank reactors
pH control	Polycarbonate reactors
Corrosion monitoring	All
Temperature monitoring	All
Level sensing and control	Storage tanks, reboilers and condensers, batch or continuous stirred tank reactors

illustrate examples of some of the kinds of considerations that are required in the design of the physical facilities to minimize the chance of a phosgene release.

5.3.1 Equipment

Materials of Construction--

The two most important considerations in selecting materials for phosgene service are the temperature and moisture content of the phosgene. The temperature is important because phosgene decomposes to carbon monoxide and chlorine at high temperatures, and most metals will ignite at a given temperature in the presence of chlorine if the temperature is high enough. The moisture content is also critical because, though dry phosgene is noncorrosive, moist or wet phosgene hydrolyzes to hydrochloric acid which is very corrosive to most metals.

Dry (anhydrous) phosgene is generally not considered corrosive. Table 5-2 shows a list of metals compatible with anhydrous phosgene. Compatible non-metals include acid resistant linings (ceramics and carbon blocks), enamel on cast iron or glass-lined steel, porcelain, and granite (8). Incompatible non-metals include most polymeric resins such as polyethylene, polypropylene, polyvinyl chloride, and polyvinyl fluoride (24).

Wet phosgene is very corrosive to most metals. In all storage vessels, the contamination of phosgene by water must be avoided (8,16). Where wet phosgene is unavoidable or likely, the materials of construction must be carefully chosen. Steel, pure copper, or cast iron are not satisfactory. Corrosion resistant metals such as tantalum, nickel-copper, or silver are required (24,25).

Vessels--

Storage vessels for phosgene service in the U.S. include 150-pound cylinders, one-ton containers, and bulk storage vessels. Because of the

TABLE 5-2. COMMON METALS REPORTED AS RESISTANT TO CHEMICAL ATTACK BY ANYHDROUS PHOSGENE

Pure Iron
Cast Iron
Carbon Steel
Stainless Steel
Copper
Nickel
Copper-nickel Alloys
Monel
Hastelloys
Aluminum
Lead
Platinum
Platinum Alloys
Silver
Gold

Source: Adapted from Reference 25.

relatively large inventories contained in phosgene storage vessels, they represent one of the most hazardous parts of the phosgene system. As a result, a variety of safety features are incorporated into phosgene storage vessels to protect against possible containment failure. These were described in Section 3.3.

Due to the extreme toxicity of phosgene, the release of any significant quantity of phosgene must be avoided. Release prevention considerations for all vessels include prevention of: overpressure, overfilling, overheating, and corrosion. With liquid phosgene, overfilling and overheating are especially important because of the large coefficient of thermal expansion associated with liquid chlorine.

An overpressure relief venting system provides overpressure protection on bulk storage vessels. The relief system should be sized for flashing liquid caused by:

- Fire exposure;
- Thermal expansion;
- Internal reaction/decomposition; and
- Excess supply rates.

The pressure relief considerations discussed for bulk storage vessels also apply to phosgene process vessels except that there is a greater likelihood of two-phase flow in these cases. The effect of two-phase flow on relief device design should be taken into account and could result in a design different from that specified for relief devices on phosgene storage systems. Much research has been done and continues to be conducted in this area by the Design Institute for Emergency Relief Systems (DIERS) (26).

It should be noted that while these devices are designed to prevent a catastrophic sudden release of vessel contents, a significant release of phosgene to the air could still occur. Protection from such an event might be

achieved if the relief device discharge were routed to a caustic scrubber. Scrubber protection systems are discussed in Subsection 5.4 of this manual.

For vessels used to transport phosgene (i.e., 150-pound cylinders and one-ton containers), no means of containing a phosgene discharge is available. Therefore, these vessels do not possess any form of pressure relief device. Without overpressure protection, great care must be taken in transporting and storing these vessels. Exposure to temperatures above 125°F must be avoided (3,8).

Prevention of overfilling can be accomplished using level sensing devices, pressure relief devices, and adequately trained personnel. Level sensing devices for phosgene service must be selected while taking into account the corrosiveness of phosgene, especially in contact with moisture. Relief devices for overfilling may be the same or similar to those used for gas pressure relief. The overfill relief would discharge to an overflow tank or other suitable receiver.

If cooling to a condenser or exothermic reactor is lost, overpressure may occur. Thus, it is necessary to use pressure relief devices to protect against leaks and ruptures caused by the overpressure. Relief protection is also necessary in the event of a fire.

In addition to venting provisions, the containers should have valve arrangements which allow the vessel to be isolated from the process to which the phosgene is being fed. In addition, concerns about overpressurization and corrosion dictate that moisture be excluded from the tanks. Tanks should not be situated in standing water and care should be taken to prevent exposure to moist air such as applying a moisture proof material to the outside of the vessel. External corrosion can be important since air always contains moisture and minor leaks could lead to acidic atmospheres.

A further concern is backflow of material into the storage vessels. When phosgene is being absorbed in a liquid, the potential exists for the liquid to be drawn back into the phosgene container. Such backflow can be prevented by a vacuum-breaking device or a barometric leg, check valves, and positive displacement pumps, or combination of the above. Another way this is prevented is to use an intermediate process feed vessel of limited inventory between the process and the main phosgene storage vessel. Should any backflow occur only a limited phosgene inventory is involved.

Careful attention should be given to vessel corrosion; vessels in phosgene service should be constructed of suitable materials of construction with adequate corrosion allowances. Special attention should be given to welds and to external corrosion under insulation.

Piping--

As with phosgene vessels, phosgene pipework design must reflect the pressure, temperature, and corrosion concerns associated with the use of phosgene. There are some general guidelines for piping systems. The first is simplicity of design; the number of joints and connections should be minimized. In addition to being securely supported, horizontal pipe runs should be sloped, with drainage provided at the low points for use when the piping has been temporarily out of service to ensure there is no water in the lines. Piping should be constructed to allow room for thermal expansion of the pipe and should be protected from possible exposure to fire and high temperatures. Valves should be placed so that leaking pipes and equipment may be isolated, but no section of piping that might contain phosgene should be isolatable from some form of overpressure relief or expansion chamber. This latter precaution is to prevent the possibility of blocked-in liquid phosgene from causing a rupture from thermal expansion.

Isolation of vessels and other phosgene process equipment may also be required for maintenance. In some cases, a single valve is insufficient to ensure complete isolation, and the use of slip plates or a double block and

bleed arrangement may be necessary. Because of the potential for releasing trapped phosgene, proper training is essential to ensure safe operation of these isolation techniques.

For phosgene applications, Schedule 80 seamless steel piping with seamless fittings is commonly used (8). Pipe no smaller than 3/4-inch nominal size should be used (8). An alternative to seamless steel pipe is double-walled pipe. This provides an added degree of protection since the outer pipe provides containment in the event that the inner pipe carrying the phosgene should rupture or leak. Double-walled piping is currently being used by several phosgene manufacturers (27).

A significant concern in liquid phosgene lines is overpressure due to thermal expansion of the phosgene if the liquid is blocked in, or pressure pulses (i.e., "water" hammer) caused by rapid valve closure. These pressures can sometimes rupture the pipes. As stated above, relief valves or expansion chambers can be used to prevent a rupture. An expansion chamber typically consists of a rupture disc and a receiver chamber which can hold about 20-30% of the capacity of the protected line. The chamber is equipped with a pressure indicator or alarm switch set to indicate its actuation. The chamber should be constructed in accordance with Section VIII of the ASME Code for Unfired Pressure Vessels. Sudden pressure pulses can be avoided by selecting valves which do not close abruptly.

Many of the considerations for piping also apply to valves. Valves for phosgene service should be strong enough to withstand the expected pressure, resistant to corrosion, easy to remove and maintain, and should have a leak-tight gland or be inherently leakproof diaphragm or bellow-sealed valves.

Ball and plug valves must be designed so that excess pressure in the body cavity (as well as in the ball or plug) will relieve spontaneously toward the high pressure side. This is accomplished by providing a relief hole in the valve body (or the ball or plug) which bypasses the upstream seat. Modified

valves such as these must indicate the flow direction on the valve body. The valve stem seals should be externally adjustable to stop stem leakage, and the stem should not be removable while the valve is in service. All valves must be supplied and maintained dry as well as grease- and oil-free.

Check-valves are used in phosgene service to prevent backflow. Because of the corrosiveness of phosgene when moisture is present, spring-loaded or gravity-operated check valves may not be suitable to prevent backflow. Instead, as is recommended for chlorine, power-operated control valves with suitable instrumentation may be preferable for primary service with a check valve backup.

Excess flow valves are used in phosgene vessels and areas where, if there is the potential for an accidental discharge of liquid, such a discharge can be reduced or prevented. For example, in the event that a liquid discharge line is broken, the resulting high flow rate causes the valve to close.

Process Machinery--

Process machinery refers to rotating or reciprocating equipment that may be used in the transfer or processing of phosgene. This includes pumps and compressors which may be used to move liquid or gaseous phosgene where gas pressure padding for moving the phosgene is insufficient or inappropriate.

Pumps--Many of the concerns and considerations for phosgene piping and valves also apply to pumps. To assure that a given pump is suitable for phosgene service, the system designer should obtain information from the pump manufacturer certifying that the pump will perform properly in this application.

Pumps should be constructed with materials which are resistant to phosgene at operating temperatures and pressures. They should be installed dry and oil-free. It is especially important that their design not allow phosgene or lubricating oil to enter seal chambers where they may contact one

another. Net positive suction head (NPSH) considerations are especially important for phosgene since pumping the liquid near its boiling point may be common (phosgene is a gas at typical ambient conditions). The pump supply tank should have high and low level alarms; the pump should be interlocked to shut off at low supply level or low discharge pressure. External pumps should be situated inside a diked area and should be accessible in the event of a tank leak.

In many cases, the potential for seal leakage rules out the use of rotating shaft seals. One solution is to use pump types which isolate the seals from the process stream. Another solution is to use pump types which eliminate shaft seals altogether such as canned-motor, vertical extended-spindle submersible, magnetically-coupled, and diaphragm (29).

Canned motor pumps are centrifugal units in which the motor housing is integral with the pump casing. Here, the process liquid actually serves as the bearing lubricant. An alternative concept is the vertical pump often used on storage tanks. Vertical pumps consist of a submerged impeller housing connected by an extended drive shaft to the motor. The advantages of this arrangement are that the shaft seal is above the maximum liquid level (and is therefore not made wet by the pumped liquid) and the pump is self priming because the liquid level is above the impeller.

Vertical pumps should be provided with double-packed seal chambers which are designed to prevent contact of phosgene and any reactive material. Seal gas should be dry, oil-free, and inert to phosgene. The seal gas pressure should be at least 10 psi over tank pressure, and a seal gas backup system be considered.

Magnetically-coupled pumps replace the drive shaft with a rotating magnetic field as the pump-motor coupling device. Diaphragm pumps are positive displacement units in which a reciprocating flexible diaphragm drives the fluid. This arrangement eliminates exposure of packing and seals to the

pumped liquid. Because of the probability of eventual diaphragm failure, the use of diaphragm pumps should be carefully considered in view of this hazard potential.

Centrifugal pumps often have a recycle loop back to the feed container which prevents overheating in the event that the pump is deadheaded (i.e., the discharge valves close). Deadheading is a special concern with positive displacement pumps. To prevent rupture, positive displacement pumps commonly have a pressure relief valve on the outlet directed back to the pump suction.

Compressors--Phosgene compressors include reciprocating, centrifugal, liquid-ring rotary, and non-lubricated screw compressors. Detailed descriptions of these compressors may be found in the technical literature (30).

Like pumps, compressors have the potential for overheating and shaft seal leakage. Heat sources in a compressor include the heat of compression as well as the heat generated through mechanical friction. Overheating in phosgene compressors is a particular concern because phosgene corrosion increases with increasing temperature. Most multistaged compressors are equipped with intercoolers which limit heating and increase compressor efficiency by reducing the volume of gas entering the next compression stage. Both air and water cooling are used, but water systems must be carefully designed to prevent leakage, as even small amounts of moisture over time could lead to corrosion and eventual compressor failure.

While it is often possible to avoid using rotary shaft seals with phosgene pumps, compressors in phosgene service usually require special seals such as double labyrinth seals. These seals have a series of interlocking touch points which reduce total leakage. To further reduce leakage, the seal is pressurized with dry air. In the event of deadheading, a compressor discharge can have a pressure relief mechanism which vents to the compressor inlet or to a scrubber system. The former appears to be satisfactory for a short term downstream flow interruption. Where a sustained interruption might

occur before the compressor could be shut down, relief to a scrubber system seems preferable.

Miscellaneous Equipment--

Pressure Relief Devices--For storage vessels, a common relief valve is of angle body construction with a closed bonnet and a screwed cap over the adjusting screw. These valves normally are used in combination with a rupture disc of an appropriate material of construction or a breaking pin assembly. Typical valve construction materials include a nickel-copper body; a nickel-plated steel spring; and nickel-copper or nickel-chromium-molybdenum alloy nozzle, disc adjusting ring, nozzle ring, and spindle guide. The inlet flange should be Class 300 and the outlet flange should be Class 150 or 300. Other types of pressure relief devices may be acceptable as long as they are constructed of materials suitable for phosgene service and meet the general requirements of the ASME boiler and Pressure Vessel Code, Section VIII, Division 1.

Rupture discs are constructed of phosgene resistant materials such as silver, tantalum, or impervious graphite. Impervious graphite rupture discs fragment upon overpressure and therefore should not be used in conjunction with relief valves. Connections smaller than two inches can be screwed, flanged or socket-welded; connections two inches or larger should be flanged or butt-welded. The flanges should be constructed of forged carbon steel and be rated in accordance with their associated piping system. Because operating pressures exceeding 70% of disc burst pressure may induce premature failure, a considerable margin is allowed when sizing rupture discs. When it is possible to draw a vacuum on the disc, supports are provided.

Process equipment should not isolated from its relief system. To provide continuous pressure relief protection, when a device is out of service for maintenance, equipment may be provided with dual relief systems, each sized to provide the total required flow capacity. Piping and valves are arranged so

that one of the systems always provides protection. Block valves installed between a vessel and its relief device should have a full port area that is at least equal to that of the pressure relief device inlet. These valves are locked open or have handles removed when the protected vessel is in use. If the discharge is to be piped to a closed disposal system, such as a scrubber, the pressure drop caused by the additional piping must be considered and the relief device sized accordingly.

Instrumentation--A primary consideration for instrumentation in phosgene service is corrosion resistance. For example, diaphragm pressure switches usually have a diaphragm constructed of a nickel-copper alloy. The upper body seal is steel, and the lower body seal is nickel-copper alloy. Direct reading pressure gauges often have a nickel-copper alloy bourdon tube. The pressure range for both types of pressure measurement devices should be twice the operating pressure. Other instrumentation, such as temperature and flow measurement devices, also should be constructed of phosgene resistant materials.

5.3.2 Plant Siting and Layout

The siting and layout of a particular phosgene facility is a complex issue which requires careful consideration of numerous factors. These include: other processes in the area, the proximity of population centers, prevailing winds, local terrain, and potential natural external effects such as flooding. The rest of this subsection describes general considerations which might apply to siting and layout of phosgene facilities.

Siting of facilities and the layout of individual equipment within a facility should be done in a manner that minimizes personnel exposure, both plant and public, in the event of a release. Since there are also other siting considerations, there may be trade-offs between this requirement and others. The site should provide ready ingress or egress in the event of an emergency and yet also take advantage of barriers, either man-made or natural,

which could reduce the consequences of releases. Large distances between large inventories and sensitive receptors (e.g., control rooms, hazardous process units, population centers) is desirable.

Layout refers to the placement and arrangement of equipment in the process facility. Some general layout considerations include the following:

- Large inventories of phosgene should be kept away from sources of fire or explosion hazard;
- Excessive vehicular traffic should be avoided near phosgene process or storage areas wherever possible;
- Where such traffic is necessary, precautions should be taken to reduce the chances for vehicular collisions with equipment, especially pipe racks carrying phosgene across or next to roadways;
- Equipment and piping containing phosgene preferably should not be located adjacent to other piping which is under high pressure or temperature, or which carries flammable materials when this can be avoided;
- Storage facilities should be segregated from the main process unless the hazards of pipe transport outweigh the hazard of the storage tank for site-specific cases; and
- Storage should also be situated away from control rooms, offices, utilities, and laboratory areas when possible.

Various techniques are available for formally assessing a plant layout and should be considered when planning high hazard facilities handling phosgene. These techniques provide for a systematic evaluation of key siting and layout factors (1).

Because heat increases phosgene corrosiveness and causes thermal expansion of liquid phosgene, measures should be taken to situate piping, storage vessels, and other phosgene equipment to minimize heat exposure. Hot process piping, equipment, steam lines, and other sources of direct or radiant heat should be avoided.

In the event of an emergency, there should be multiple means of access to the facility for emergency vehicles and crews. Storage vessel shut off valves should be readily accessible. Containment for liquid storage tanks can be provided by diking. In phosgene facilities, diking of storage tanks can serve two purposes. It can keep spilled flammable liquids from collecting near phosgene-containing equipment and possibly involving the phosgene equipment in a fire or explosion. It can also contain phosgene spilled as a liquid, which can reduce the evaporation rate as the flashing phosgene self cools. It is possible to equip a diked area to allow drainage of liquid phosgene to an underground containment sump. This sump could be vented to a scrubber system for safe discharge. A full containment system using a specially constructed building vented to a scrubber is another possible option. This type of secondary containment could be considered for large volume, liquid phosgene storage tanks. However, secondary hazards with such a system, such as inadvertent worker exposure in a closed area, require extreme care in layout and design.

5.4 PROTECTION TECHNOLOGIES

This subsection describes four types of protection technologies for containment and neutralization. These are:

- Enclosures;
- Scrubbers;
- Incinerators; and
- Flares.

More detailed information on these systems is presented in a companion manual on control technologies, part of this prevention reference manual series.

5.4.1 Enclosures

Enclosures are secondary containment structures which capture any phosgene spilled or vented from storage or process equipment, thereby preventing immediate discharge of the chemical to the environment. The enclosures contain the spilled liquid or gas until it can be transferred to other containment, such as an extra tank, discharged at a controlled rate which would not be injurious to people or the environment, or transferred at a controlled rate to other devices, such as scrubbers, for neutralization.

The use of specially designed enclosures for either phosgene storage or process equipment does not appear to be widely practiced. However, one facility has enclosed several individual unit operations involved in the manufacture of phosgene and is considered state of the art in protection (27). The location of toxic operations in the open air has been mentioned favorably in the literature, along with the opposing idea that sometimes enclosure may be appropriate (1). The desirability of enclosure depends partly on the frequency with which personnel must be involved with the equipment. A common design rationale for not having an enclosure where toxic materials are used is to prevent the accumulation of toxic concentrations of a chemical within a work area. However, if the issue is protecting the community from accidental releases, then total enclosure may be appropriate. Enclosures should be equipped with continuous monitoring equipment and alarms to sound whenever a release of phosgene within the enclosure is detected.

Special care must be taken when an enclosure is built around pressurized equipment. It may not be practical to design an enclosure to withstand the pressures associated with the sudden failure of a pressurized vessel. The enclosure would probably fail as a result of the pressure created from such a release and could create an additional hazard. In these situations, it may be

determined that an enclosure is not appropriate. If an enclosure is built around pressurized equipment, then it should be equipped with some type of explosion protection, such as rupture plates that are designed to fail before the entire structure fails. While some phosgene would be released, the amount would be less than without the enclosure, and the enclosure would still serve well when the release was not a rupture event.

The type of containment structures that appear to be suitable for phosgene are concrete block or concrete panel buildings, or bunkers. An enclosure preferably would be gas tight to the outside, but would have a ventilation system to draw outside air into the enclosure, and then vent through a scrubber. The bottom section of a building used for stationary storage containers could be liquid tight to retain any liquid phosgene that might be spilled. Buildings around rail tank cars used for storage do not lend themselves well to completely effective liquid containment. However, containment could be accomplished if the floor of the building is excavated several feet below the track level while the tracks are supported at grade in the center.

While the use of enclosures for secondary containment of phosgene spills or releases is not known to be widely used, it can be considered as a possible protection technology for areas near especially sensitive receptors.

5.4.2 Scrubbers

Scrubbers are a traditional method for absorbing toxic gases from process streams. These devices can be used to control phosgene releases from vents and pressure relief discharges from storage equipment, process equipment, or secondary containment enclosures.

Phosgene discharges could be contacted with an aqueous scrubbing medium in any of several types of scrubbing devices. An alkaline solution is required to achieve effective absorption because phosgene absorption rates with

water alone would require unreasonably high liquid-to-gas ratios. However, water scrubbing could be used in a makeshift scrubber in an emergency if an alkaline solution were not available. Typical minimum quantities of alkaline solutions for an emergency scrubber to accommodate standard container sizes of phosgene are presented in Table 5-3.

Types of scrubbers that might be appropriate include spray towers, packed bed scrubbers, and venturis. Other types of special designs might be suitable, but complex internals subject to corrosion do not seem to be advisable. Whichever type of scrubber is selected, a key consideration for emergency systems is the design flow rate to be used. A conservative design would use the maximum rate that would be expected from an emergency. This rate can be calculated for relief valve discharges, open lines, and equipment ruptures. Table 5-4 presents some efficiency data for a phosgene packed bed scrubbing system. Note, however, that these concentrations are much lower than those that may be experienced during an emergency discharge.

Whatever type of scrubber is selected, a complete system would include the scrubber itself, a liquid feed system, and reagent makeup equipment. If such a system is used as protection against emergency releases, consideration must be given to how it would be activated in time to respond to an emergency load. One approach used in some process facilities is to maintain a continuous circulation of scrubbing liquor through the system. This may be practical where the emergency scrubber also serves as a routine vent scrubber. For many facilities this would not be practical and the scrubber system might be tied into a trip system which would turn it on when needed. However, with this system, a quantity of phosgene would be released prior to actuation of the scrubber (i.e., starting up a blower and turning on the flow of liquid).

The scrubbing system must be designed so as not to present excessive resistance to the flow of an emergency discharge. The pressure drop should be only a small fraction of the total pressure drop through the emergency discharge system. In general, at the liquid-to-gas ratios required for effective

TABLE 5-3. TYPICAL QUANTITIES OF ALKALINE SOLUTION FOR PHOSGENE SCRUBBING

Container Capacity	Caustic Soda	
	100% (lb)	Water, (gal)
150	486	720
2,000	6,540	9,660

Source: Reference 14.

TABLE 5-4. EXAMPLE OF PACKED BED SCRUBBER EFFICIENCIES FOR PHOSGENE RELEASES

Inlet Flow Rate (scfm)	Inlet Concentration (ppm)	Primary Scrubber Outlet Concentration (ppm)	Primary Scrubber Efficiency (%)	Secondary Scrubber Outlet Concentration (ppm)	Total System Efficiency (%)
1.7	88	1.17	98.67	0.019	99.98
4.5	237	0.761	99.68	0.015	99.99+
16.3	864	9.31	98.92	0.132	99.98
17.2	911	6.46	99.29	0.050	99.99+
31.6	1,671	26.8	98.40	0.470	99.97

Source: Adapted from Reference 31.

scrubbing, spray towers have the lowest, and venturis the highest, pressure drops. While packed beds may have intermediate pressure drops at proper liquid-to-gas ratios, excessive ratios or plugging can increase the pressure drop substantially. However, packed beds have higher removal efficiencies than spray towers or venturis.

In addition, the scrubber system must be designed to handle the "shock wave" generated during the initial stages of the release. This is particularly important for packed bed scrubbers since there is a maximum pressure with which the gas can enter the packed section without damaging the scrubber internals.

Design of emergency scrubbers can follow standard techniques discussed in the literature, carefully taking into account the additional considerations just mentioned. An example of the sizing of an emergency packed bed scrubber is presented in Table 5-5. This example provides some idea of the size of a typical emergency scrubber for various flow rates. This is an example only and should not be used as the basis for an actual system which might differ based on site specific requirements.

Another approach is the drowning tank, where the phosgene vent is routed to the bottom of a large tank of uncirculating caustic. The drowning tank does not have the high contact efficiency of the other scrubber types. However, it can provide substantial capacity on demand as long as the back pressure of the hydrostatic head does not create a secondary hazard, by impeding an overpressure relief discharge, for example. In addition, precautions must be taken to prevent backflow of the scrubbing liquid through the lines to a phosgene containing vessel since explosions can occur. Such an event could occur as a result from overflowing of the scrubber.

5.4.3 Incinerators

Incineration is a traditional method of destroying toxic vapor from process streams. Such devices can be used for control of phosgene releases

TABLE 5-5. EXAMPLE OF PERFORMANCE CHARACTERISTICS FOR AN EMERGENCY PACKED BED SCRUBBER FOR PHOSGENE

Basis: Inlet stream of 50% $COCl_2$ in 50% air. Constant gas flow per unit cross-sectional area of 200 scfm/ft^2.

Packing: 2-inch plastic Intalox® saddles.

Pressure Drop: 0.5-inch water column

Scrubbing Medium: 8% (wt) NaOH solution

Removal Efficiency, %	50	90
Liquid-to-Gas Ratio (gal/thousand scf)		
--at flooding	260	260
--operating	140	140
Packed Height, ft.	1.2	4.0

Column Diameter and Corresponding Gas Flow Rates for Both Removal Efficiencies

Column Diameter (ft)	Flow Rate (scfm)
1.0	160
2.0	630
3.0	1,400

Source: Reference 32.

from vents and pressure relief discharges, from process equipment, or from secondary containment enclosures.

Phosgene discharges can be mixed with fuel and air in a thermal oxidation unit in order to convert the toxic vapor to carbon monoxide and chlorine, since phosgene decomposes to these product gases at a temperature of 1,472°F (8). An additional problem arises in that hydrogen chloride formed during incineration is highly corrosive and thus the incineration system would have to be constructed of corrosion-resistant materials. Also, an acid-gas scrubber is needed to remove the hydrogen chloride and chlorine from the vent gases before being released, although these gases are much less toxic than phosgene at comparable concentrations.

Considerations for activation in the event of an emergency load of hazardous vapor are similar to those associated with scrubber systems discussed above.

5.4.4 Flares

Flares are devices routinely used in the chemical process industries to destroy toxic waste gases. A flare is a section of vertical piping with a specially designed combustion tip. Flares are distinguished from other process combustion devices such as incinerators by their design to handle extreme flow rate variations and their unenclosed combustion zone. As with incineration, phosgene discharges could be mixed with fuel and air to convert the toxic vapor to carbon monoxide and chlorine at a temperature of 1,472°F (8).

A total flare system consists of collection piping, a seal pot, a liquid knock-out vessel, and the flare itself. Two basic types of flares are elevated flares and enclosed ground flares. The elevated flare is usually designed to handle larger flows than the ground flare, and is more likely to be used for high volume upset or emergency flaring situations. The ground flare is more likely to be used for smaller volume, routine process venting.

Basic design requirements for flares burning phosgene are:

- The ability to operate safely over a wide range of flow rates and varying compositions;
- Have acceptable emissions of radiant heat and noise; and
- Achieve acceptable destruction efficiency for phosgene.

The ability of flares to accommodate large variations in flow rate is an important consideration in using them for protection against accidental phosgene releases. Depending on the size of a flare relative to a potential release, the accidental release flow rate may constitute a large or small fraction of the total flare flow rate and correspondingly could have a significant or relatively minor effect on the instantaneous total flow rate and flare performance.

There are two possible ways a flare system can be used to protect against accidental phosgene releases. The first is to use an existing flare system. The second is to use a dedicated "emergency" system. Whether a dedicated flare or shared flare is used depends on site specific considerations. A shared flare may be advantageous for several reasons. A dedicated flare system for infrequent emergency use may be difficult to safely maintain in full working condition. A shared flare may allow connection to an existing system. With a shared flare, however, design for emergency conditions must ensure that a large release of phosgene does not overwhelm the flare and lead to flame blowout, or that the pressure from the toxic emergency release does not cause a backflow into other process units tied into the flare collection piping.

Flares can be useful protection against accidental releases of phosgene. However, because of potentially dangerous secondary hazards, their use requires a thorough analysis for each specific application. In essence, a

flare system is a pipe transporting flammable gases to a flame at the exit. As long as the flame remains at the end of the pipe, the system operates safely. The flame can enter the pipe if oxygen is present above a certain concentration in the fuel. In a dedicated flare system, the entire collection network would have to be continually purged to prevent the risk of an explosion when an accidental release occurred.

Backpressure in the discharge line for an emergency phosgene release is a concern in discharging to a flare system. Since the flare collection system operates under a positive pressure (above atmospheric), release rates from an emergency relief valve will be less than discharge to the atmosphere. In some instances, it is conceivable that the slight delay in reducing the pressure in a vessel may cause tank damage. This may be especially important when rupture disks blow. A sudden overpressurization of the flare collection system due to a massive accidental release could damage the pipes or potentially affect the venting of other process units. Table 5-6 summarizes the factors that need to be considered to prevent accidental chemical releases when using a flare system.

5.5 MITIGATION TECHNOLOGIES

If, in spite of all precautions, a large release of phosgene were to occur, the first priority would be to rescue workers in the immediate vicinity of the accident and evacuate persons from downwind areas. The source of the release should be determined, and the leak should be stopped, if this is possible. The next primary concern becomes reducing the consequences of the released chemical to the plant and the surrounding community. Reducing the consequences of an accidental release of a hazardous chemical is referred to as mitigation. Potential mitigation technologies include such measures as physical barriers, water sprays and fogs, and foams where applicable. The purpose of a mitigation technique is to divert, limit, or disperse the chemical that has been spilled or released to the atmosphere in order to reduce the atmospheric concentration and the area affected by the chemical. The mitigation technology chosen for a particular chemical depends on the specific

TABLE 5-6. IMPORTANT CONSIDERATIONS FOR USING FLARES TO PREVENT ACCIDENTAL CHEMICAL RELEASES

- Maximum flow rate - will it cause a flame blowout?
- Possibility of air, oxygen, or other oxidant entering system?
- Is gas combustible - will it smother the flare?
- Will any reactions occur in collection system?
- Can liquids enter the collection system?
- Will liquids flash and freeze, overload knockout drum or cause rain fire?
- Is back pressure of collection system dangerous to releasing vessel?
- Is releasing vessel gas pressure or temperature dangerous to collection system?
- Will acids or salts enter collection system?
- Will release go to an enclosed ground or elevated flare?
- If toxic is not destroyed, what are the impacts on surrounding community?

properties of the chemical including its flammability, toxicity, reactivity, and those properties which determine its dispersion characteristics in the atmosphere.

If a release occurs from a pressurized liquid phosgene storage tank above the boiling point, a quantity of liquid will immediately flash off as vapor, while the remaining liquid may be cooled to the normal boiling point of 45.5°F. Heat transfer from the air and ground will result in further vaporization of the released liquid. Since the phosgene accidentally released from a refrigerated storage tank is already at or below its normal boiling point, a comparable quantity of vapor will not flash off, as with the pressurized release discussed above, but heat transfer from the environment will cause evaporation and the formation of a vapor cloud. It is therefore desirable to minimize the area available for heat transfer to a liquid spill which in turn will minimize the rate of evaporation. Mitigation technologies which are used to reduce the rate of evaporation of a released liquefied gas include secondary containment systems such as impounding basins and dikes.

A post release mitigation effort requires that the source of the release be accessible to trained plant personnel. Therefore, the availability of adequate personnel protection is essential. Personnel protection will typically include such items as portable breathing air and chemically resistant protective clothing.

5.5.1 Secondary Containment Systems

Specific types of secondary containment systems include excavated basins, natural basins, earth, steel, or concrete dikes, and high impounding walls. The type of containment system best suited for a particular storage tank or process unit will depend on the risk associated with an accidental release from that location. The inventory of phosgene and its proximity to other portions of the plant and to the community should be considered when selecting a secondary containment system. The secondary containment system should have

the ability to contain spills with a minimum of damage to the facility and its surroundings and with minimum potential for escalation of the event.

Secondary containment systems for phosgene storage facilities commonly consist of one of the following:

- An adequate drainage system underlying the storage vessels which terminates in an impounding basin having a capacity as large as the largest tank served; and

- A diked area, with a capacity as large as the largest tank served.

These measures are designed to prevent the accidental discharge of liquid phosgene from spreading to uncontrolled areas.

The most common type of containment system is a low wall dike surrounding one or more storage tanks. Generally, no more than three tanks are enclosed within one diked area to reduce risk. Dike heights usually range from three to twelve feet depending on the area available to achieve the required volumetric capacity. The dike walls should be liquid tight and able to withstand the hydrostatic pressure and temperature of a spill. Low wall dikes may be constructed of steel, concrete or earth. If earthen dikes are used, care must be taken to ensure that the phosgene cannot leak through the dike. Piping should be routed over dike walls, and penetrations through the walls should be avoided if possible. Vapor fences may be situated on top of the dikes to provide additional vapor containment. If there is more than one tank in the diked area, the tanks should be situated on berms above the maximum liquid level attainable in the impoundment.

A low wall dike can effectively contain the liquid portion of an accidental release and keep the liquid from entering uncontrolled areas. By preventing the liquid from spreading, the low wall dike can reduce the surface area of the spill. Reducing the surface area will reduce the rate of evaporation.

The low wall dike will partially protect the spill from wind; this can reduce the rate of evaporation. A dike with a vapor fence will provide extra protection from wind and will be even more effective at reducing the rate of evaporation.

A low wall dike will not reduce the impact of a gaseous phosgene release. A dike also creates the potential for phosgene and trapped water to mix in the dike, which may accelerate the rate of evaporation and form highly corrosive hydrochloric and hydrochlorous acids. If materials that would react violently with phosgene are stored within the same diked area then the dike will increase the potential for mixing the materials in the event of a simultaneous leak. A dike also limits access to the tank during a spill.

A remote impounding basin is well suited to storage systems where more than one tank is served and a relatively large site is available. The flow from a phosgene spill is directed to the basin by dikes and channels under the storage tanks which are designed to minimize contact of the liquid with other tanks and surrounding facilities. Because of the high vapor pressure of phosgene, the trenches that lead to the remote impounding basin as well as the basin itself should be covered to reduce the rate of evaporation. Additionally, the impounding basin should be located near the tank area to minimize the amount of phosgene that evaporates as it travels to the basin.

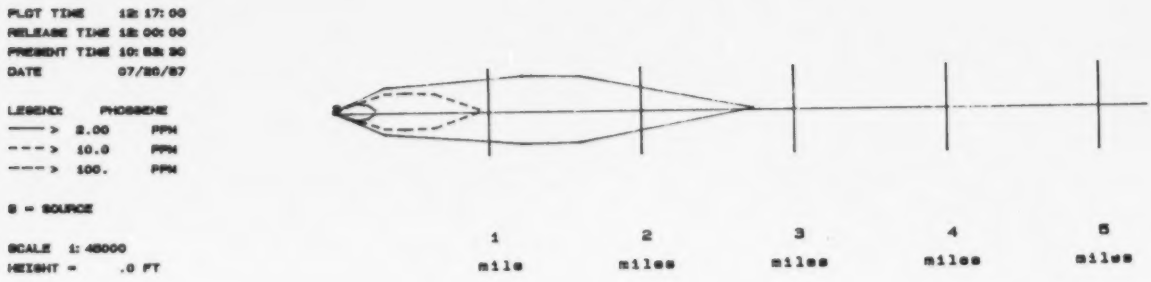
This type of system has several advantages. The spilled liquid is removed from the immediate tank area. This allows access to the tank during the spill and reduces the probability that the spilled liquid will damage the tank, piping, electrical equipment, pumps or other equipment. In addition, the covered impoundment will reduce the rate of evaporation from the spill by protecting the spill from wind or heating from sunlight.

A limitation of a remote impounding basin is that there is still the potential for water or other incompatible materials to be trapped in the impoundment and mix with the incoming phosgene. Remote impounding basins do not reduce the impact of a gaseous phosgene release.

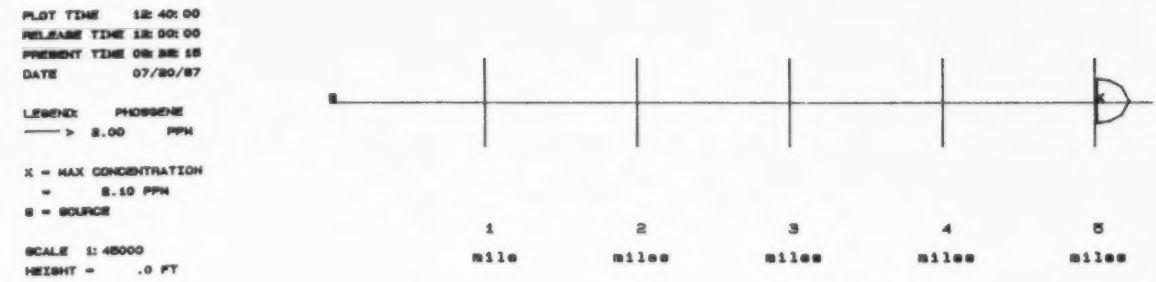
Although a limited number of chemical facilities use them, high wall impoundments may be a good secondary containment choice for selected systems. Circumstances which may warrant their use include limited storage site area, the need to minimize vapor generation rates, and/or the tank must be protected from external hazards. Maximum vapor generation rates will generally be lower for a high wall impoundment than for low wall dikes or remote impoundments because of the reduced surface contact area. These rates can be further reduced with the use of insulation on the wall and floor in the annular space. High impounding walls may be constructed of low temperature steel, reinforced concrete, or prestressed concrete. A weather shield may be provided between the tank and wall with the annular space remaining open to the atmosphere. The available area surrounding the storage tank will dictate the minimum height of the wall. For high wall impoundments, the walls may be designed with a volumetric capacity greater than that of the tank to provide vapor containment. Increasing the height of the wall also raises the elevation of any released vapor.

One disadvantage of these dikes is that the high walls around a tank may hinder routine external observation. Furthermore, the closer the wall is to the tank, the more difficult it becomes to access the tank for inspection and maintenance. As with low wall dikes, piping should be routed over the wall if possible. The closeness of the wall to the tank may necessitate placement of the pump outside of the wall, in which case the outlet (suction) line will have to pass through the wall. In such a situation, a low dike encompassing the pipe penetration and pump may be provided, or a low dike may be placed around the entire wall.

An example of the effect of diking as predicted by one vapor dispersion model is shown in Figure 5-1 (3). With diking, the predicted maximum IDLH exposure occurs at a distance of 14,500 feet at 17 minutes after release. Without diking, the predicted maximum IDLH exposure occurs at a distance of 27,700 feet at 40 minutes after exposure.



Release from a tank surounded by a 25 ft. diameter dike.
Elapsed Time: 17 minutes



Release from a tank with no dike.
Elapsed Time: 40 minutes

Common Release Conditions

Storage Temperature = 85°F
Storage Pressure = 17 psig
Ambient Temperature = 85°F

Wind Speed = 10 mph
Atmospheric Stability Class = C
Quantity Released = 5000 gallons through a 2-inch hole

Figure 5-1. Computer model simulation showing the effect of diking on the vapor cloud generated from a release of liquified phosgene.

One further type of secondary containment system is one which is structurally integrated with the primary system and forms a vapor tight enclosure around the primary container. Many types of arrangements are possible. A double walled tank is an example of such an enclosure. These systems may be considered where protection of the primary container and containment of vapor for events not involving foundation or wall penetration failure are of greatest concern. Drawbacks of an integrated system are the greater complexity of the structure, the difficulty of access to certain components, and the fact that complete vapor containment cannot be guaranteed for all potential events.

Provision should be made for drainage of rainwater from diked areas. This will involve the use of sumps and separate drainage pumps, since direct drainage to storm-water sewers would presumably allow any spilled phosgene to follow the same route. Alternately, a sloped rain hood may be used over the diked area which could also serve to direct the rising vapors to a single release point (33). The ground within the enclosure should be graded to cause the spilled liquid to accumulate at one side or in one corner. This will help to minimize the area of ground to which the liquid is exposed and from which it may gain heat. In areas where it is critical to minimize vapor generation, surface insulation may be used in the diked area to further reduce heat transfer from the environment to the spilled liquid. The floor of an impoundment should be sealed with a clay blanket to prevent the phosgene from seeping into the ground; percolation into the ground causes the ground to cool more quickly, increasing the vapor generation rate. Absorption of the phosgene into water in the soil would also release additional heat.

5.5.2 Flotation Devices and Foams

Other possible means of reducing the surface area of spilled phosgene include placing impermeable flotation devices on the surface or applying water-based foams. Placing an impermeable flotation device over a spilled chemical is a direct approach for containing toxic vapors with nearly 100 percent efficiency. However, being able to use such devices requires acquisi-

tion in advance of a spill and storage until needed, and in all but small spills deployment may be difficult. The additional material and dispersal equipment costs are a major deterrent to their use.

The use of foams in vapor hazard control has been demonstrated for a broad range of volatile chemicals. Unfortunately, it is difficult to accurately quantify the benefits of foam systems, because the effects will vary as a function of the chemical spilled, foam type, spill size, and atmospheric conditions. With regard to liquefied gases, it has been found that with some materials, foams have a net positive effect, but with others, foams may exaggerate the hazard. Information is not currently available on the use of foams in controlling phosgene vapor.

In general, when a foam is first applied, an increase in the boil-off rate is observed which would cause a short-term increase in the downwind concentration. The initial foam cover may be destroyed by violent boiling, in which case a second application is necessary. Once a continuous layer is formed, a net positive effect will be achieved in the downwind area. The reduction in downwind concentration is a result of both increased dilution with air, because of a reduced vaporization rate, and the increased buoyancy of the vapor cloud. This latter effect is a result of the vapor being warmed as it rises through the blanket by heat transfer from the foam and by the heat of solution in water; the warmed vapor cloud will have greater buoyancy and will disperse in an upward direction more rapidly.

The extent of the downwind reduction in concentration will depend on the type of foam used. Regardless of the type of foam used, the slower the drainage rate of the foam, the better its performance will be. A slow draining foam will spread more evenly, show more resistance to temperature and pH effects, and collapse more slowly. The initial cost for a slow draining foam may be higher than for other foams, but a cost-effective system will be realized in superior performance.

Even if the vaporization rate of phosgene is substantially reduced within a short time after a spill, a vapor cloud may still be formed which poses a serious threat downwind. Dispersion and/or removal of the phosgene vapor in the atmosphere is the subject of the following section.

5.5.3 Mitigation Techniques for Phosgene Vapor

The extent to which the escaped phosgene vapor can be removed or dispersed in a timely manner will be a function of the quantity of vapor released, the ambient conditions, and the physical characteristics of the vapor cloud. The behavior and characteristics of the phosgene cloud depend on a number of factors. These include the physical state of the phosgene before its release, the location of the release, and the atmospheric and environmental conditions. Many possibilities exist concerning the shape and motion of the vapor cloud, and a number of predictive models of dispersion have been developed. Phosgene has a higher specific gravity than air; the vapor cloud will spread laterally and remain close to the ground.

One means of dispersing and removing toxic vapors from the air is with the use of a mild aqueous alkaline spray system such as caustic or an ammonia injected water spray system which would act as a neutralizing agent. The spray medium can be applied to the vapor cloud with hand-held hoses and/or stationary water-spray barriers. Effectiveness of spray system depends on distance of the nozzle from the point of release, the spray pattern, and rate of application. If water sprays are used to mitigate phosgene vapors from a diked area containing spilled liquid phosgene, great care must be taken not to direct water into the liquid phosgene itself.

In general, techniques used to disperse or control vapor emissions should emphasize simplicity and reliability. In addition to the mitigation techniques mentioned above, physical barriers such as buildings and rows of trees will help to contain the vapor cloud and control its movement. Additional information or mitigation methods can be found in a manual on control technologies for mitigation, part of this manual series.

5.6 OPERATION AND MAINTENANCE PRACTICES

Quality hardware, contained mechanical equipment, and protective devices all increase plant safety; however, they must be supported by the safety policies of management and by proper operation and maintenance practices. This section describes briefly how management policy and training, operation, and maintenance procedures contribute to the prevention of accidental phosgene releases. Within the phosgene industry, these procedures and practices vary because of individual differences among firms. For this reason, the following subsections focus primarily on fundamental principles and do not attempt to define specific policies and procedures.

5.6.1 Management Policy

Management has a fundamental role in the control of industrial hazards and the prevention of accidental releases. Management establishes the broad policies and procedures which influence the implementation and execution of specific hazard control measures. It is important that these management policies and procedures be designed to match the level of risk in the facilities where they will be used. Most organizations have a formal safety policy.

Many make policy statements to the effect that safety must rank equally with other company functions such as production and sales. The effectiveness of any safety program, however, is determined by a company's commitment to it, as demonstrated throughout the management structure. Specific goals must be derived from the general safety policy and supported by all levels of management. Safety and loss prevention should be an explicit management objective. Ideally, management should establish the specific safety performance measures, provide incentives for attaining safety goals, and commit adequate company resources to safety and hazard control.

In the context of accident prevention, management is responsible for (1,34):

- Ensuring worker competency;
- Developing and enforcing standard operating procedures;
- Adequately documenting policy and procedures;
- Communicating and promoting feedback regarding safety issues;
- Providing for identification, assessment, and control of hazards; and
- Regular plant audits and verification that specified procedures and practices are being followed.

Additional discussion on the responsibilities of management can be found in a manual on control technologies for prevention, protection, and mitigation, part of this manual series (20).

5.6.2 Operator Training

The performance of operating personnel is significant in the prevention of accidental phosgene releases. Many case studies documenting industrial incidents note the contribution of human error to accidental releases (1). Release incidents may be caused by using improper routine operating procedures, by insufficient knowledge of process variables and equipment, by lack of knowledge about emergency or upset procedures, by failure to recognize critical situations, and in some cases by direct physical mistake (e.g., turning the wrong valve). A comprehensive operator training program can decrease the potential for accidents resulting from such causes.

Operator training can include a wide range of activities and a broad spectrum of information. Training, however, is distinguished from education in that it is specific to particular tasks. While general education is important and beneficial, it is not a substitute for specific training. The content of a specific training program depends on the type of industry, the nature of the processes used, the operational skills required, the characteristics of the plant management system, and tradition.

Some general characteristics of quality industrial training programs include:

- Establishment of good working relations between management and personnel;
- Definition of trainer responsibilities and training program goals;
- Use of documentation, classroom instruction, and field training (in some cases supplemented with simulator training);
- Inclusion of procedures for normal start-up and shutdown, routine operations, and upsets, emergencies, and accidental releases; and
- Frequent supplemental training and the use of up-to-date training materials.

In many instances, training is carried out jointly by plant managers and a training staff selected by management. In others, management is solely responsible for maintaining training programs. In either case, responsibilities should be explicitly designated to ensure that the quality and quantity of training provided is adequate. Training requirements and practices can be expected to differ between small and large companies, partly because of resource needs and availability, and partly because of differences in employee turnover.

A list of the aspects typically involved in the training of process operators for routine process operations is presented in Table 5-7.

Emergency training includes topics such as:

- Recognition of alarm signals;
- Performance of specific functions (e.g., shutdown switches);
- Use of specific equipment;
- Actions to be taken on instruction to evacuate;
- Fire fighting; and
- Rehearsal of emergency situations.

Aspects specifically addressed in safety training include (1,34):

- Hazard recognition and communication;
- Actions to be taken in particular situations;
- Available safety equipment and locations;
- When and how to use safety equipment;
- Use and familiarity with documentation such as,
  - plant design and operating manuals,
  - company safety rules and procedures,
  - procedures relevant to fire, explosion, accident, and health hazards,
  - chemical property and handling information; and

TABLE 5-7. ASPECTS OF TRAINING PROGRAMS FOR ROUTINE PROCESS OPERATIONS

Process goals, economics, constraints, and priorities
Process flow diagrams
Unit Operations
Process reactions, thermal effects
Control systems
Process materials quality, yields
Process effluents and wastes
Plant equipment and instrumentation
Equipment identification
Equipment manipulation
Operating procedures
Equipment maintenance and cleaning
Use of tools
Permit systems
Equipment failure, services failure
Fault administration
Alarm monitoring
Fault diagnosis
Malfunction detection
Communications, recordkeeping, reporting

Source: Reference 1.

- First aid and CPR.

Although emergency and safety programs typically focus on incidents such as fires, explosions, and personnel safety, it is important that prevention of accidental chemical releases and release responses be addressed as part of these programs.

Much of the type of training discussed above is also important for management personnel. Safety training gives management the perspective necessary to formulate good policies and procedures, and to make changes that will improve the quality of plant safety programs. Lees suggests that training programs applied to managers include or define (33):

- Overview of technical aspects of safety and loss prevention approach;
- Company systems and procedures;
- Division of labor between safety personnel and managers in with respect to training; and
- Familiarity with documented materials used by workers.

5.6.3 Maintenance and Modification Practices

Plant maintenance is necessary to ensure the structural integrity of chemical processing equipment; modifications are often necessary to allow more effective production. However, since these activities are also a primary source of accidental release incidents, proper maintenance and modification practices are an important part of accidental release prevention. Use of a formal system of controls is perhaps the most effective way of ensuring that maintenance and modification are conducted safely. In many cases, control systems have had a marked effect on the level of failures experienced (1).

Permit systems and up-to-date maintenance procedures minimize the potential for accidents during maintenance operations. Permit-to-work systems control maintenance activities by specifying the work to be done, defining individual responsibilities, eliminating or protecting against hazards, and ensuring that appropriate inspection and testing procedures are followed.

Maintenance permits originate with the operating staff. Permits may be issued in one or two stages. In one-stage systems, the operations supervisor issues permits to the maintenance supervisor, who is then responsible for his staff. Two-stage systems involve a second permit issued by the maintenance supervisor to his work force (1).

Another form of maintenance control is the maintenance information system. Ideally, these systems should log the entire maintenance history of equipment, including preventative maintenance, inspection and testing, routine servicing, and breakdown or failure maintenance. This type of system is also used to track incidents caused by factors such as human error, leaks, and fires, including identification and quantification of failures responsible for hazardous conditions, failures responsible for downtime, and failures responsible for direct repair costs.

Accidental releases are frequently the result of some aspect of plant modification. Accidents result when equipment integrity and operation are not properly assessed following modification, or when modifications are made without updating corresponding operation and maintenance instructions. In these situations, it is important that careful assessment of the modification results has a priority equal to that of getting the plant on-line.

For effective modification control, there must be established procedures for authorization, work activities, inspection, and assessment, complete documentation of changes, including the updating of manuals, and additional training to familiarize operators with new equipment and procedures (1,34).

Formal procedures and checks on maintenance and modification practices must be established to ensure that such practices enhance rather than adversely affect plant safety As with other plant practices, procedure development and complete documentation are necessary. However, training, attitude, and the degree to which the procedures are followed also significantly influence plant safety and release prevention.

The use and availability of clearly defined procedures collected in maintenance and operating manuals is crucial for the prevention of accidental releases. Well-written instructions should give enough information about a process that the worker with hands-on responsibility for operating or maintaining the process can do so safely, effectively, and economically. These instructions not only document the path to the desired results, but also are the basis for most industrial training programs (35,36). In the chemical industry, operating and maintenance manuals vary in content and detail. To some extent, this variation is a function of process type and complexity; however, in many cases it is a function of management policy. Because of their importance to the safe operation of a chemical process, these manuals must be as clear, straightforward, and complete as possible. In addition, standard procedures should be developed and documented before plant start-up, and appropriate revisions should be made throughout plant operations.

Operation and maintenance may be combined or documented separately. Procedures should include startup, shutdown, hazard identification, upset conditions, emergency situations, inspection and testing, and modifications (1). Several authors think industrial plant operating manuals should include (1,34,35,36):

- Process descriptions;
- A comprehensive safety and occupational health section;
- Information regarding environmental controls;

- Detailed operating instructions, including startup and shutdown procedures;
- Upset and emergency procedures;
- Sampling instructions;
- Operating documents (e.g., logs, standard calculations);
- Procedures related to hazard identification;
- Information regarding safety equipment;
- Descriptions of job responsibilities; and
- Reference materials.

Plant maintenance manuals typically contain procedures not only for routine maintenance, but also for inspection and testing, preventive maintenance, and plant or process modifications. These procedures include specific items such as codes and supporting documentation for maintenance and modifications (e.g., permits-to-work, clearance certificates), equipment identification and location guides, inspection and lubrication schedules, information on lubricants, gaskets, valve packings and seals, maintenance stock requirements, standard repair times, equipment turnaround schedules, and specific inspection codes (e.g., for vessels and pressure systems) (1). Full documentation of the maintenance required for protective devices is a particularly important aspect of formal maintenance systems.

The preparation of operating and maintenance manuals, their availability, and the familiarity of workers with their contents are all important to safe plant operations. The objective, however, is to maintain this safe practice throughout the life of the plant. Therefore, as processes and conditions are modified, documented procedures must also be modified.

5.7 CONTROL EFFECTIVENESS

It is difficult to quantify the control effectiveness of preventive and protective measures to reduce the probability and magnitude of accidental releases. Preventive measures, which may involve numerous combinations of process design, equipment design, and operational measures, are especially difficult to quantify because they reduce the probability of a release rather than a physical quantity of chemical. Protective measures are more analogous to traditional pollution control technologies. Thus they may be easier to quantify in terms of their efficiency in reducing a quantity of chemical that could be released.

Preventive measures reduce the probability of an accidental release by increasing the reliability of process systems operations and equipment. Control effectiveness can thus be expressed for both of the qualitative improvements achieved and quantitative improvements as probabilities. Table 5-8 summarizes what appears to be major design, equipment, and operational measures applicable to the primary hazards identified for the phosgene applications in the United States. The items listed in Table 5-8 are for illustration only and do not necessarily represent a satisfactory control option for all cases. These control options appear to reduce the risk associated with an accidental release when viewed from a broad perspective. However, there are undoubtedly specific cases where these control options will not be appropriate. Each case must be evaluated individually. A presentation of more information about reliability in terms of probabilities is discussed in the manual on control technologies, part of this prevention reference manual series.

5.8 ILLUSTRATIVE COST ESTIMATES FOR CONTROLS

This section presents cost estimates for different levels of control and for specific release prevention and protection measures for phosgene storage and process facilities that might be found in the U.S. These are examples only and costs are intended to show relative relationships. Appropriate control measures and costs for actual facilities are site specific.

TABLE 5-8. EXAMPLES OF MAJOR PREVENTION AND PROTECTION MEASURES FOR PHOSGENE RELEASES

Hazard Area	Prevention/Protection
OPERATIONAL RELATED:	
Human error	Increased training and supervision; use of checklists; use of automatic systems
Vehicular collisions	Location; physical barriers; warning signs; training
PROCESS RELATED:	
Water contamination in feed streams	Continuous moisture monitoring; backflow prevention; pad gas drying
Methane or hydrogen contamination in carbon monoxide feed to phosgene reactor	Continuous hydrogen and methane monitoring
Excess phosgene rates	Enhanced flow control; limited over-design of feed systems; fail-shut control valves
Overheated reactor	Redundant temperature sensing and alarms; interlocked phosgene feed shut-off;
Cooling media flow control	Redundant temperature sensors; interlock flow switch to shut off phosgene feed on loss of cooling
Heating media flow control	Redundant temperature sensors; interlock flow switch to shut off phosgene feed on loss of heating
Overpressure	Enhanced pressure relief (non-isolatable, adequate-sized, no discharge restrictions, safe discharge point)

(Continued)

TABLE 5-8. (Continued)

Hazard Area	Prevention/Protection
PROCESS RELATED: (Continued)	
Direct relief discharges to atmosphere	Emergency scrubber system; tank enclosures; incinerator system
External fire	Siting away from flammables; refrigeration systems; heat shield
EQUIPMENT RELATED:	
Corrosion	Inspections, maintenance, and corrosion monitoring
Flexible connection failures	Minimized use; higher quality components; operator training in proper assembly; more frequent inspections and maintenance; replacement of copper with Monel®
Fusible plug failure	Inspection/certification; storage in a containment building
Major tank or line rupture in storage	Diking; enclosure with scrubber; corrosion monitoring; overpressure protection; siting away from flammables and mechanical damage; inspection and non-destructive testing
Other vessel failure	Adequate pressure relief; inspection and maintenance; corrosion monitoring; siting away from fire and mechanical damage

5.8.1 Prevention and Protection Measures

Preventive measures reduce the probability of an accidental release from a process or storage facility by increasing the reliability of both process systems operations and equipment. Along with an increase in the reliability of a system is an increase in the capital and annual costs associated with incorporating prevention and protection measures into a system. Table 5-9 presents costs for some of the major design, equipment, and operational measures applicable to the primary hazards identified in Table 5-8 for phosgene applications in the United States.

5.8.2 Levels of Control

Prevention of accidental releases relies on a combination of technological, administrative, and operational practices as they apply to the design, construction, and operation of facilities where hazardous chemicals are used and stored. Inherent in determining the degree to which these practices are carried out is their costs. At a minimum, equipment and procedures should be in accordance with applicable codes, standards, and regulations. However, additional measures can be taken to provide extra protection against an accidental release.

The levels of control concept provides a means of assigning costs to increased levels of prevention and protection. The minimum level is referred to as the "Baseline" system. This system consists of the elements required for normal safe operation and basic prevention of an accidental release of hazardous material.

The second level of control is "Level 1". "Level 1" includes the baseline system with added modifications such as improved materials of construction, additional controls, and generally more extensive release prevention measures. The costs associated with this level are higher than the baseline system costs.

TABLE 5-9. ESTIMATED TYPICAL COSTS OF SOME PREVENTION AND PROTECTION MEASURES FOR PHOSGENE RELEASES

Prevention/Protection Measure	Capital Cost (1986 $)	Annual Cost (1986 $/yr)
Continuous moisture monitoring	7,500-10,000	
Replacement of copper lines with Monel®	150-200	20-25
Pressure relief		
- relief valve	1,000-2,000	120-250
- rupture disk	1,000-1,200	120-150
Level sensor		
- liquid level gauge	1,500-2,000	175-250
- load cell	10,000-15,000	1,300-1,900
Flow control loop	4,000-6,000	500-750
Temperature sensor	250-400	30-50
pH control	7,500-10,000	900-1,300
Interlock system for feed shut-off	1,500-2,000	175-250
Alarm system	250-500	30-75
Diking		
- 3 ft high	1,200-1,500	150-175
- top of tank height	7,000-7,500	850-900
Corrosion monitoring[a]		200-400
Increased inspections and maintenance[b]		250-500

[a]Based on 10-20 hr @ $20/hr.

[b]Based on 12.5-25 hr @ $20/hr.

The third level of control is "Level 2.". This system incorporates both the "Baseline" and "Level 1" systems with additional modifications such as alarm and interlock systems designed specifically for the prevention of an accidental release. The extra accidental release prevention measures incorporated into "Level 2" are reflected in its cost, which is much higher than that of the baseline system.

When comparing the costs of the various levels of control, it is important to realize that higher costs do not necessarily imply improved safety. The measures must be applied correctly. Inappropriate modifications or add-ons may not make a system safer. Each added control option increases the complexity of a system. In some cases the hazards associated with the increased complexity may outweigh the benefits derived from the particular control option. Proper design and construction along with proper operational practices are needed to assure safe operation.

These estimates are for illustrative purposes only. It is doubtful that any specific installation would find all of the control options listed in these tables appropriate for their purposes. An actual system is likely to incorporate some items from each of the levels of control and also some control options not listed here. The purpose of these estimates is to illustrate the relationship between cost and control, and is not to provide an equipment checklist.

Levels of control cost estimates were prepared for a 57.9 ton fixed phosgene storage tank system with a 10,000 gallon capacity and a 2,000 gallon polycarbonate reactor system. These systems are representative of storage and process facilities that might be found in the United States.

5.8.3 Summary of Levels of Control

Table 5-10 presents a summary of the total capital and annual costs for each of the three levels of controls for the phosgene storage system and the polycarbonate reaction system. The costs presented correspond to the systems

TABLE 5-10. SUMMARY COST ESTIMATES OF POTENTIAL LEVELS OF CONTROLS FOR PHOSGENE STORAGE TANK AND POLYCARBONATE REACTOR

System	Level of Control	Total Capital Cost (1986 $)	Total Annual Cost (1986 $/yr)
Phosgene Storage Tank; 58 ton Fixed Storage Tank with 10,000 Gallon Capacity.	Baseline	431,000	51,000
	Level No. 1	506,000	60,000
	Level No. 2	1,278,000	150,000
Polycarbonate Reactor System 2,000 Gallon Reactor	Baseline	360,000	44,000
	Level No. 1	400,000	49,000
	Level No. 2	682,000	83,000

described in Table 5-11 and Table 5-12. Each of the level costs include the cost of the basic system plus any added controls. Specific cost information and breakdown for each level of control for both the storage and process facilities are presented in Tables 5-13 through 5-18.

5.8.4 Equipment Specifications and Detailed Costs

Equipment specifications and details of the capital cost estimates for the phosgene storage and the polycarbonate reactor systems are presented in Table 5-19 through 5-26.

5.8.5 Methodology

Format for Presenting Cost Estimates--

Tables are provided for control schemes associated with storage and process facilities for phosgene showing capital, operating, and total annual costs. The tables are broken down into subsections comprising vessels, piping and valves, process machinery, instrumentation, and procedures and practice. The presentation of the costs in this manner allows for easy comparison of costs for specific items, different levels, and different systems.

Capital Cost--All capital costs presented in this report are shown as total fixed capital costs. Table 5-27 defines the cost elements comprising total fixed capital as it is used here.

The computation of total fixed capital as shown in Table 5-27 begins with the total direct cost for the system under consideration. This total direct cost is the total direct installed cost of all capital equipment comprising the system. Depending on the specific equipment item involved, the direct capital cost was available or was derived from uninstalled equipment costs by computing costs of installation separately. To obtain the total fixed capital cost, other costs obtained by utilizing factors are added to the total direct costs.

TABLE 5-11. EXAMPLE OF LEVELS OF CONTROL FOR PHOSGENE STORAGE TANK[a]

Process: 58 Ton Fixed Phosgene Storage Tank - 10,000 gallon

Controls	Baseline	Level No. 1	Level No. 2
Flow:	Single check valve on tank process feed line.	Add second check valve.	Add a reduce-pressure device[b] with internal air gap and relief vent to containment tank or scrubber.
Temperature:	Temperature indicator and alarm.	Add remote indicator.	Add redundant sensors and alarms.
Pressure:	Single pressure relief valve, vent to limited scrubber.	Add second relief valve, secure non-isolatable. Vent to scrubber. Add alarm.	Add redundant alarms. Add rupture disks under relief valve. Provide local pressure indication on space between disk and valve.
Quantity:	Local level indicator and alarm.	Add remote indicator.	Add redundant alarms and high-low level interlock shut-off for both inlet and outlet lines.
Location:	Away from traffic, flammables and other hazardous processes.	Same	Same
Materials of Construction:	Carbon steel.	Carbon steel with increased corrosion allowance (1/8 inch).	Monel®
Vessel[c]:	Tank pressure specification: 150 psig.	Tank pressure specification: 250 psig.	Tank pressure specification: 375 psig.

(Continued)

TABLE 5-11. (Continued)

Process: 58 Ton Fixed Phosgene Storage Tank - 10,000 gallon

Controls	Baseline	Level No. 1	Level No. 2
Piping:	Schedule 80 carbon steel.	Schedule 80 Monel®.	Schedule 80 Monel®.
Process Machinery:	Centrifugal pump, carbon steel, double mechanical seal.	Centrifugal pump, Monel® construction, double mechanical seal.	Magntically-coupled centrifugal pump, Monel® construction.
Enclosures:	None	None	Steel building.
Diking:	3 ft. high dike.	Top of tank height, 10 ft.	3 ft. high dike.
Scrubbers:	Alkaline scrubber.	Same	Same
Mitigation:	None	Alkaline sprays and barriers.	Same

[a]The examples in this table are appropriate for many, but not all applications. This is only an exemplary system. Design must be suited to fit the service.

[b]A reduced-pressure device is a modified double check valve.

[c]Note that tank pressure specification will be a function of maximum operating pressure. These valves are chosen only as representative examples.

TABLE 5-12. EXAMPLE OF LEVELS OF CONTROL FOR POLYCARBONATE REACTOR SYSTEM

Controls	Baseline	Level No. 1	Level No. 2
Process:	Use of alklaline stabilizing system.	Provide back-up mixing.	Use of interlocks and back-cooling systems.
Temperature:	Provide temperature control with local temperature indication and alarm.	Add redundant sensors and alarms.	Add remote indicators and alarms.
Pressure:	Provide remote control with remote pressure sensing. Single pressure relief valve to scrubber.	Add redundant remote pressure sensing and control with alarms. Add second relief valve, vent to scrubber.	Add rupture disks under relief valves.
Flow:	Provide remote flow control on phosgene, caustic and amine feed lines.	Add redundant flow control loops.	Add automatic shut-off of feed.
Mixing:	Provide adequate mixing.	Add agitation detection system.	Interlock phosgene feed shut-off with loss of mixing.
Composition:	pH monitoring and control.	Same	Same
Material of Construction:	Carbon steel.	Carbon steel with increased corrosion protection; 1/8 inch.	Monel®
Vessel:	Reactor pressure specification: 150 psig.	Reactor pressure specification: 250 psig.	Reactor pressure specification: 375 psig.
Piping:	Schedule 80 carbon steel.	Schedule 80 Monel®.	Same

(Continued)

TABLE 5-12. (Continued)

Controls	Baseline	Level No. 1	Level No. 2
Protective Barrier:	Curbing around reactor.	3 ft. high retaining wall.	Same
Enclosure:	None	None	Steel building.
Scrubber:	Alkaline scrubber.	Same	Same

TABLE 5-13. CAPITAL AND ANNUAL COSTS ASSOCIATED WITH BASELINE PHOSGENE STORAGE SYSTEM

	Capital Cost (1986 $)	Annual Cost (1986 $/yr)
Vessels:		
Storage Tank	131,000	15,000
Piping and Valves:		
Pipework	2,300	270
Check Valve	280	35
Globe Valves (5)	3,200	370
Relief Valve	2,000	230
Process Machinery:		
Centrifugal Pump	4,000	470
Instrumentation:		
Local Temperature Indicator	1,900	220
Temperature Alarm	380	45
Pressure Gauges (2)	1,485	170
Pressure Alarm	380	45
Liquid Level Indicator	1,900	220
Level Alarm	380	45
Scrubber:		
Alkaline Scrubber	280,000	33,000
Diking:		
Three-Foot High Concrete Dike	1,400	160
Procedures and Practices:		
Visual Tank Inspection (external)		15
Visual Tank Inspection (internal)		60
Relief Valve Inspection		15
Piping Inspection		300
Piping Maintenance		120
Valve Inspection		30
Valve Maintenance		350
TOTAL COSTS	431,000	51,000

TABLE 5-14. CAPITAL AND ANNUAL COSTS ASSOCIATED WITH LEVEL 1 PHOSGENE STORAGE SYSTEM

	Capital Cost (1986 $)	Annual Cost (1986 $/yr)
Vessels:		
Storage Tank	187,000	2,200
Piping and Valves:		
Pipework	12,000	1,500
Check Valves (2)	570	65
Globe Valves (5)	3,200	370
Relief Valve (2)	4,000	470
Process Machinery:		
Centrifugal Pump	6,400	750
Instrumentation:		
Local Temperature Indicator	1,900	220
Remote Temperature Indicator	2,200	260
Temperature Alarm	380	45
Temperature Sensor	380	45
Pressure Gauges (2)	1,485	170
Pressure Alarm	380	45
Liquid Level Indicator	1,900	220
Remote Level Indicator	2,200	260
Level Alarm	380	45
Scrubber:		
Alkaline scrubber	280,000	33,000
Diking:		
Ten-Foot High Concrete Dike	7,600	880
Procedures and Practices:		
Visual Tank Inspection (external)		15
Visual Tank Inspection (internal)		60
Relief Valve Inspection		15
Piping Inspection		300
Piping Maintenance		120
Valve Inspection		30
Valve Maintenance		350
TOTAL COSTS	513,000	61,000

TABLE 5-15. CAPITAL AND ANNUAL COSTS ASSOCIATED WITH LEVEL 2 PHOSGENE STORAGE SYSTEM

	Capital Cost (1986 $)	Annual Cost (1986 $/yr)
Vessels:		
Storage Tank	932,000	109,000
Piping and Valves:		
Pipework	12,000	1,500
Reduced Pressure Device	1,000	120
Globe Valves (5)	3,200	370
Relief Valve (2)	4,000	470
Rupture Disks (2)	1,100	130
Process Machinery:		
Centrifugal Pumps	19,000	2,200
Instrumentation:		
Local Temperature Indicator	1,900	220
Remote Temperature Indicator	2,200	260
Temperature Alarms (2)	760	90
Temperature Sensor	380	45
Pressure Gauges (2)	1,485	170
Pressure Alarms (2)	760	90
Liquid Level Indicator	1,900	220
Remote Level Indicator	2,200	260
Level Alarms (2)	760	90
High-low Level Shutoff	1,900	220
Scrubber:		
Alkaline Scrubber	280,000	33,000
Enclosures:		
Steel Building	10,000	1,200
Procedures and Practices:		
Visual Tank Inspection (external)		15
Visual Tank Inspection (internal)		60
Relief Valve Inspection		15
Piping Inspection		300
Piping Maintenance		120
Valve Inspection		30
Valve Maintenance		350
TOTAL COSTS	1,278,000	150,000

TABLE 5-16. CAPITAL AND ANNUAL COSTS ASSOCIATED WITH BASELINE POLYCARBONATE REACTOR SYSTEM

	Capital Cost (1986 $)	Annual Cost (1986 $/yr)
Vessels:		
Reactor	42,000	5,000
Piping and Valves:		
Pipework	2,200	270
Globe Valves (10)	6,200	750
Relief Valve	2,000	240
Process Machinery:		
Centrifugal Pump	3,900	470
Instrumentation:		
Local Temperature Indicator	1,800	220
Temperature Alarm	380	45
Temperature Control:		
Controller	1,800	220
Sensor	380	45
Control Valve	2,700	320
Remote Pressure Indicator	2,200	260
Pressure Alarm	380	45
Flow Control Loops (3):		
Controller	5,400	650
Flowmeter	6,800	850
Control Valve	8,400	1,000
Scrubber System:	272,000	33,000
Diking:		
Curbing Around Reactor	910	110
Procedures and Practices:		
Visual Tank Inspection (external)		15
Visual Tank Inspection (internal)		60
Relief Valve Inspection		15
Piping Inspection		300
Piping Maintenance		120
Valve Inspection		30
Valve Maintenance		350
TOTAL COSTS	360,000	44,000

TABLE 5-17. CAPITAL AND ANNUAL COSTS ASSOCIATED WITH LEVEL 1 POLYCARBONATE REACTOR SYSTEM

	Capital Cost (1986 $)	Annual Cost (1986 $/yr)
Vessels:		
Reactor	63,000	7,500
Piping and Valves:		
Pipework	12,000	1,400
Glove Valves (10)	6,200	750
Relief Valves (2)	4,000	480
Process Machinery:		
Centrifugal Pump	6,200	750
Instrumentation:		
Local Temperature Indicator	1,800	220
Temperature Alarms (2)	760	90
Temperature Sensor	380	45
Temperature Control:		
Controller	1,800	220
Sensor	380	45
Control Valve	2,700	320
Remote Pressure Indicators (2)	4,300	520
Pressure Control:		
Controller	1,800	220
Sensor	380	45
Control Valve	2,700	320
Pressure Alarms (2)	760	90
Flow Control Loops (3):		
Controller	5,400	650
Flowmeter	1,400	850
Control Valve	8,400	1,000
Agitation Detection System and Alarm	1,800	220
Scrubber System:	272,000	33,000
Diking:		
Three-Foot High Retaining Wall	1,300	200
Procedures and Practices:		
Visual Tank Inspection (external)		15
Visual Tank Inspection (internal)		60
Relief Valve Inspection		15
Piping Inspection		300
Piping Maintenance		120
Valve Inspection		30
Valve Maintenance		350
TOTAL COSTS	400,000	49,000

TABLE 5-18. CAPITAL AND ANNUAL COSTS ASSOCIATED WITH LEVEL 2 POLYCARBONATE REACTOR SYSTEM

	Capital Cost (1986 $)	Annual Cost (1986 $/yr)
Vessels:		
Reactor	313,000	38,000
Piping and Valves:		
Pipework	12,000	1,400
Glove Valves (10)	6,200	750
Relief Valves (2)	4,000	480
Rupture Disks (2)	1,100	130
Process Machinery:		
Centrifugal Pump	19,000	2,200
Instrumentation:		
Remote Temperature Indicator	2,200	260
Temperature Alarms (2)	780	90
Temperature Sensor	350	45
Temperature Control:		
Controller	1,800	220
Sensor	390	45
Control Valve	2,800	320
Remote Pressure Indicators (2)	4,300	520
Pressure Control:		
Controller	1,800	220
Sensor	390	45
Control Valve	2,800	320
Pressure Alarms (2)	780	90
Flow Control Loops (3):		
Controller	5,400	650
Flowmeter	7,000	850
Control Valve	8,400	1,000
Flow Interlock Systems (2)	3,900	430
Agitation Detection System and Alarm	1,800	220
Scrubber System:	272,000	33,000
Diking:		
Three-Foot High Retaining Wall	1,600	200

(Continued)

TABLE 5-18. (Continued)

	Capital Cost (1986 $)	Annual Cost (1986 $/yr)
Enclosure:		
Steel Building	8,400	1,000
Procedures and Practices:		
Visual Tank Inspection (external)		15
Visual Tank Inspection (internal)		60
Relief Valve Inspection		15
Piping Inspection		300
Piping Maintenance		120
Valve Inspection		30
Valve Maintenance		350
TOTAL COSTS	682,000	83,000

TABLE 5-19. EQUIPMENT SPECIFICATIONS ASSOCIATED WITH PHOSGENE STORAGE SYSTEM

Equipment Item	Equipment Specification	Reference
VESSEL:		
Storage tank	Baseline: 10,000 gal. carbon steel, 150 psig rating Level #1: 10,000 gal. carbon steel with 1/8 inch corrosion protection, 250 psig pressure rating Level #2: 10,000 gal., Monel® 375 psig pressure rating	37, 38, 39, 40
PIPING & VALVES		
Pipework	Baseline: 100 ft. of 1 in. Schedule 80 Level #1: 100 ft. of 1 in. Schedule 80 Monel® Level #2: 100 ft. of 1 in. Schedule 80 Monel®	41
Check Valve	1 in. vertical lift check valve, Monel® construction	38, 42
Globe Valve	1 in. ANSI Class 300, Monel® construction	37, 38, 42
Relief Valve	1 in. x 2 in., ANSI Class 300 inlet and outlet flange, angle body, closed bonnet with screwed cap, Monel® body and trim	38
Reduced Pressure Device	Double check valve type device with internal air gap and relief valve	37
Rupture Disk	1 in. Monel® and carbon steel holder	37, 39, 43
PROCESS MACHINERY:		
Centrifugal Pump	Baseline: 100 gpm. Carbon steel construction, double mechanical seal Level #1: Monel® construction, double mechanical seal Level #2: Magnetically-coupled centrifugal pump, Monel® construction	38, 44

(Continued)

TABLE 5-19. (Continued)

Equipment Item	Equipment Specification	Reference
INSTRUMENTATION		
Local Temperature Indicator	Thermocouple, thermowell, and electronic indicator /recorder	37, 38, 45
Remote Temperature Indicator	Transmitter and associated electronic indicator/recorder	37, 45
Temperature Sensor	Thermocouple and associated thermowell	37, 38, 45
Temperature Alarm	Indicating and audible alarm	44, 38, 46, 47
Pressure Gauge	Diaphragm sealed, Type 316 stainless steel diaphragm, 0-100 psig rating	37, 38, 45
Pressure Alarm	Indicating and audible alarm	38, 46, 47
Level Alarm	Indicating and audible alarm	38, 46, 47
Level Indicator	Electrical differential pressure type indicator	37, 46
High-Low Level Shut-off	Solenoid valve, switch and relay system	37, 38, 45, 46
ENCLOSURE:		
Building	Level #2: 26-gauge steel walls and roof, door, ventilation system	46
DIKING:	Baseline: 6 in. concrete walls, 3 ft. high Level #1: 10 in. concrete walls, top of tank height (10 ft.)	46
Scrubber:	Spray tower, Monel® construction, alkaline sprays, 6 ft. x 18 ft.	48

TABLE 5-20. MATERIAL AND LABOR COSTS ASSOCIATED WITH BASELINE PHOSGENE STORAGE SYSTEM

	1986 Dollars				
	Materials Cost	Labor Cost	Direct Costs	Indirect Costs	Capital Cost
Vessels:					
Storage Tank	61,000	27,000	88,000	31,000	131,000
Piping and Valves:					
Pipework	500	1,000	1,550	540	2,300
Check Valves	160	30	190	65	280
Globe Valves (5)	2,000	150	2,150	750	3,200
Relief Valve	1,300	50	1,350	470	2,000
Process Machinery:					
Centrifugal Pump	1,900	800	2,700	950	4,000
Instrumentation:					
Local Temperature Indicator	1,000	250	1,250	440	1,900
Temperature Alarm	200	50	250	90	380
Pressure Gauges (2)	800	200	1,000	350	1,485
Pressure Alarm	200	50	250	90	380
Liquid Level Indicator	1,000	250	1,250	440	1,900
Level Alarm	200	50	250	90	380
Scrubber System:					
Alkaline Scrubber	130,000	59,000	189,000	66,000	280,000
Diking:					
Three-foot High Concrete Dike	390	510	900	320	1,300
TOTAL COSTS	201,000	89,000	290,000	102,000	431,000

TABLE 5-21. MATERIAL AND LABOR COSTS ASSOCIATED WITH LEVEL 1 PHOSGENE STORAGE SYSTEM

	1986 Dollars				
	Materials Cost	Labor Cost	Direct Costs	Indirect Costs	Capital Cost
Vessels:					
Storage Tank	87,000	39,000	126,000	44,000	187,000
Piping and Valves:					
Pipework	4,800	3,500	8,300	2,900	12,000
Check Valves (2)	320	60	380	140	570
Globe Valves (5)	2,000	150	2,150	750	3,200
Relief Valves (2)	2,600	100	2,700	950	4,000
Process Machinery:					
Centrifugal Pump	3,000	1,300	4,300	1,500	6,400
Instrumentation:					
Local Temperature Indicator	1,000	250	1,250	440	1,900
Remote Temperature Indicator	1,200	300	1,500	530	2,200
Temperature Alarm	200	50	250	90	380
Temperature Sensor	200	50	250	90	380
Pressure Gauges (2)	800	200	1,000	350	1,485
Pressure Alarm	200	50	250	90	380
Liquid Level Indicator	1,000	250	1,250	440	1,900
Remote Level Indicator	1,200	300	1,500	530	2,200
Level Alarm	200	50	250	90	380
Scrubber:					
Alkaline Scrubber	130,000	59,000	189,000	66,000	280,000
Diking:					
Ten-foot High Concrete Dike	2,200	2,900	5,100	1,800	7,600
TOTAL COSTS	238,000	108,000	346,000	121,000	513,000

TABLE 5-22. MATERIAL AND LABOR COSTS ASSOCIATED WITH LEVEL 2 PHOSGENE STORAGE SYSTEM

	1986 Dollars				
	Materials Cost	Labor Cost	Direct Costs	Indirect Costs	Capital Cost
Vessels:					
Storage Tank	432,000	195,000	627,000	220,000	932,000
Piping and Valves:					
Pipework	4,800	3,500	8,300	2,900	12,000
Reduced Pressure Device	800	200	1,000	350	1,500
Globe Valves (5)	2,000	150	2,150	750	3,200
Relief Valves (2)	2,600	100	2,700	950	4,000
Rupture Disks (2)	650	75	725	260	1,100
Process Machinery:					
Centrifugal Pump	9,000	3,900	12,900	4,500	19,000
Instrumentation:					
Local Temperature Indicator	1,000	250	1,250	440	1,900
Remote Temperature Indicator	1,200	300	1,500	530	2,200
Temperature Alarms (2)	400	100	500	180	760
Temperature Sensor	200	50	250	90	380
Pressure Gauges (2)	800	200	1,000	350	1,485
Pressure Alarms (2)	400	100	500	180	760
Liquid Level Indicator	1,000	250	1,250	440	1,900
Remote Level Indicator	1,200	300	1,500	530	2,200
Level Alarm (s)	400	100	500	180	760
High-Low Level Shutoff	1,000	250	1,250	440	1,900
Scrubber:					
Alkaline Scrubber	130,000	59,000	189,000	66,000	280,000
Diking:					
Three-Foot High Concrete Dike	390	520	910	320	1,400
Enclosures:					
Steel Building	4,600	2,300	6,900	2,400	10,000
TOTAL COSTS	594,000	267,000	861,000	302,000	1,278,000

TABLE 5-23. EQUIPMENT SPECIFICATIONS ASSOCIATED WITH POLYCARBONATE REACTOR SYSTEM

Equipment Item	Equipment Specification		Reference
VESSEL:			
Reactor	Baseline:	2,000 gal. carbon steel, 150 psig rating.	37, 38, 39, 40
	Level #1:	Same as baseline with added corrosion allowance, 250 psig rating.	
	Level #2:	2,000 gal. Monel® reactor 375 psig rating.	
PIPING AND VALVES:			
Pipework	Baseline:	100 ft. of 1 inch Schedule 80 carbon steel.	41
	Level #1:	100 ft. of 1 inch Schedule 80 Monel®.	
	Level #2:	Same as Level #1.	
Globe Valve	2 in. ANSI class 300, Monel® construction.		37, 38, 42
Relief Valve	1 in. x 2 in. ANSI class 300 inlet and outlet flange, angle body, closed bonnet with screwed cap, Monel® body and trim.		38
Rupture Disk	1 in. Monel® with carbon steel holder steel holder		37, 39, 43
PROCESS MACHINERY:			
Centrifugal Pump	Baseline:	Single stage, 100 gpm capacity, carbon steel construction, double mechanical seal.	37, 44
	Level #1:	Same as baseline with Monel® construction.	
	Level #2:	Magnetically-coupled centrifugal pump, Monel® construction.	

(Continued)

TABLE 5-23. (Continued)

Equipment Item	Equipment Specification	Reference
INSTRUMENTATION:		
Local Temperature Indicator	Thermocouple, thermowell, and electronic indicator	37, 38, 45
Remote Temperature Indicator	Transmitter and associated electronic indicator	37, 45
Temperature Sensor	Thermocouple and associated thermowell	37, 38, 45
Temperature Alarm	Indicating and audible alarm	37, 46, 47
Temperature Control Loop	PID controller, 1 in. globe control valve of Monel® construction, and temperature sensor.	37, 45
Pressure Control Loop	PID controller, 1 in. globe control valve of Monel® construction, pressure sensor.	37, 45
Remote Pressure Indicator	Transducer, transmitter, and electronic indicator.	37, 45
Flow Control Loop	PID controller, 1 in. globe control valve of Monel® construction, flowmeter.	37, 45
Flow Interlock System	Solenoid valve, switch, and relay system	37, 38, 46
DIKING:	Baseline: 0.5 ft. high concrete curbing Level #1 & 2: 3 ft. high concrete retaining wall	46
ENCLOSURE:	Level #2: 26 gauge steel walls and roof, door, ventilation system.	46
Scrubber:	Spray tower, Monel® construction, alkaline sprays, 6 ft. x 18 ft.	48

TABLE 5-23. (Continued)

Equipment Item	Equipment Specification	Reference
INSTRUMENTATION:		
Local Temperature Indicator	Thermocouple, thermowell, and electronic indicator	37, 38, 45
Remote Temperature Indicator	Transmitter and associated electronic indicator	37, 45
Temperature Sensor	Thermocouple and associated thermowell	37, 38, 45
Temperature Alarm	Indicating and audible alarm	37, 46, 47
Temperature Control Loop	PID controller, 1 in. globe control valve of Monel® construction, and temperature sensor.	37, 45
Pressure Control Loop	PID controller, 1 in. globe control valve of Monel® construction, pressure sensor.	37, 45
Remote Pressure Indicator	Transducer, transmitter, and electronic indicator.	37, 45
Flow Control Loop	PID controller, 1 in. globe control valve of Monel® construction, flowmeter.	37, 45
Flow Interlock System	Solenoid valve, switch, and relay system	37, 38, 46
DIKING:	Baseline: 0.5 ft. high concrete curbing Level #1 & 2: 3 ft. high concrete retaining wall	46
ENCLOSURE:	Level #2: 26 gauge steel walls and roof, door, ventilation system.	46
Scrubber:	Spray tower, Monel® construction, alkaline sprays, 6 ft. x 18 ft.	48

TABLE 5-24. MATERIAL AND LABOR COSTS ASSOCIATED WITH BASELINE POLYCARBONATE REACTOR SYSTEM

	1986 Dollars				
	Materials Cost	Labor Cost	Direct Costs	Indirect Costs	Capital Cost
Vessels:					
Reactor	20,000	9,000	29,000	7,500	42,000
Piping and Valves:					
Pipework	550	1,000	1,550	390	2,200
Globe Valves (10)	4,000	300	4,300	1,100	6,200
Relief Valve	1,300	50	1,350	340	2,000
Process Machinery:					
Centrifugal Pump	1,900	800	2,700	680	3,900
Instrumentation:					
Local Temperature Indicator	1,000	250	1,250	320	1,800
Temperature Alarm	200	50	250	90	380
Temperature Control:					
Controller	1,000	250	1,250	320	1,800
Sensor	200	50	250	90	380
Control Valve	1,500	375	1,875	470	2,700
Remote Pressure Indicator	1,200	300	1,500	380	2,200
Pressure Alarm	200	50	250	90	380
Flow Control Loops (3):					
Controller	3,000	750	3,750	940	5,400
Flowmeter	3,900	1,000	4,900	1,200	6,800
Control Valve	4,500	1,300	5,800	1,500	8,400
Scrubber System:	130,000	59,000	189,000	48,000	272,000
Diking:					
Curbing Around Reactor	500	130	630	160	910
TOTAL COSTS	175,000	75,000	250,000	64,000	360,000

TABLE 5-25. MATERIAL AND LABOR COSTS ASSOCIATED WITH LEVEL 1 POLYCARBONATE REACTOR SYSTEM

	1986 Dollars				
	Materials Cost	Labor Cost	Direct Costs	Indirect Costs	Capital Cost
Vessels:					
Reactor	30,000	13,500	43,500	11,000	63,000
Piping and Valves:					
Pipework	4,800	3,500	8,300	2,100	12,000
Globe Valves (10)	4,000	300	4,300	1,100	6,200
Relief Valves (2)	2,600	100	2,700	680	4,000
Process Machinery:					
Centrifugal Pump	3,000	1,300	4,300	1,100	6,200
Instrumentation:					
Local Temperature Indicator	1,100	250	1,250	320	1,800
Temperature Alarms (2)	400	100	500	180	760
Temperature Sensor	200	50	250	90	380
Temperature Control:					
Controller	1,000	250	1,250	320	1,800
Sensor	200	50	250	90	380
Control Valve	1,500	375	1,875	470	2,700
Remote Pressure Indicators (2)	2,400	600	3,000	760	4,300
Pressure Control:					
Controller	1,000	250	1,250	320	1,800
Sensor	200	50	250	90	380
Control Valve	1,500	375	1,875	470	2,700
Pressure Alarms (2)	400	100	500	180	760

(Continued)

TABLE 5-25. (Continued)

	1986 Dollars				
	Materials Cost	Labor Cost	Direct Costs	Indirect Costs	Capital Cost
Flow Control Loops (3):					
Controller	3,000	750	3,750	940	5,400
Flowmeter	3,900	1,000	4,900	1,200	1,400
Control Valve	4,500	1,300	5,800	1,500	8,400
Agitation Detection System and Alarm	1,000	250	1,250	310	1,800
Scrubber System:	130,000	59,000	189,000	48,000	272,000
Diking:					
Three-Foot High Retaining Wall	900	230	1,130	290	1,300
TOTAL COSTS	198,000	84,000	282,000	72,000	400,000

TABLE 5-26. MATERIAL AND LABOR COSTS ASSOCIATED WITH LEVEL 2 POLYCARBONATE REACTOR SYSTEM

	1986 Dollars				
	Materials Cost	Labor Cost	Direct Costs	Indirect Costs	Capital Cost
Vessels:					
Reactor	150,000	68,000	218,000	55,000	313,000
Piping and Valves:					
Pipework	4,800	3,500	8,300	2,900	12,000
Globe Valves (10)	4,000	300	4,300	1,100	6,200
Relief Valves (2)	2,600	100	2,700	950	4,000
Rupture Disks (2)	650	75	725	260	1,100
Process Machinery:					
Centrifugal Pump	9,000	3,900	12,900	4,500	19,000
Instrumentation:					
Remote Temperature Indicator	1,200	300	1,500	380	2,200
Temperature Alarms (2)	400	100	500	180	780
Temperature Sensor	200	50	250	90	350
Temperature Control:					
Controller	1,000	250	1,250	320	1,800
Sensor	200	50	250	90	390
Control Valve	1,500	375	1,875	470	2,800
Remote Pressure Indicators (2)	2,400	600	3,000	760	4,300
Pressure Control:					
Controller	1,000	250	1,250	320	1,800
Sensor	200	50	250	90	390
Control Valve	1,500	375	1,875	470	2,800
Pressure Alarms (2)	400	100	500	180	780

(Continued)

TABLE 5-26. (Continued)

	1986 Dollars				
	Materials Cost	Labor Cost	Direct Costs	Indirect Costs	Capital Cost
Flow Control Loops (3):					
Controller	3,000	750	3,750	940	5,400
Flowmeter	3,900	1,000	4,900	1,200	7,000
Control Valve	4,500	1,300	5,800	1,500	8,400
Flow Interlock Systems (2)	2,000	500	2,500	880	3,900
Agitation Detection System and Alarm	1,000	250	1,250	310	1,800
Scrubber System:	130,000	59,000	189,000	48,000	272,000
Diking:					
Three-Foot High Retaining Wall	900	230	1,130	290	1,600
Enclosure:					
Steel Building	4,600	1,200	5,800	1,500	8,400
TOTAL COSTS	331,000	143,000	474,000	123,000	682,000

TABLE 5-27. FORMAT FOR TOTAL FIXED CAPITAL COST

Item No.	Item	Cost
1	Total Material Cost	-
2	Total Labor Cost	-
3	Total Direct Cost	Items 1 + 2
4	Indirect Cost Items (Engineering & Construction Expenses)	0.35 x Item 3[a]
5	Total Bare Module Cost	Items (3 + 4)
6	Contingency	(0.05 x Item 5)[b]
7	Contractor's Fee	0.05 x Item 5
8	Total Fixed Capital Cost	Items (5 + 6 + 7)

[a]For storage facilities, the indirect cost factor is 0.35. For process facilities, the indirect cost factor is 0.25.

[b]For storage facilities, the contingency cost factor is 0.05. For process facilities, the contingency cost factor is 0.10.

The first group of other cost elements is indirect costs. These include engineering and supervision, construction expenses, and various other expenses such as administration expenses, for example. These costs are computed by multiplying total direct costs by a factor shown in Table 5-27. The factor is approximate, is obtained from the cost literature, and is based on previous experience with capital projects of a similar nature. Factors can have a range of values and vary according to technology area and for individual technologies within an area. Appropriate factors were selected for use in this report based on judgement and experience.

When the indirect costs are added to the total direct costs, total bare module cost is obtained. Some additional cost elements such as contractor's fee and contingency are calculated by applying and adding appropriate factors to the total bare module cost as shown in Table 5-27 to obtain the total fixed capital cost.

Annual Cost--Annual costs are obtained for each of the equipment items by applying a factor for both capital recovery and for maintenance expenses to the direct cost of each equipment item. Table 5-28 defines the cost elements and appropriate factors comprising these costs. Additional annual costs are incurred for procedural items such as valve and vessel inspections, for example. When all of these individual costs are added, the total annual cost is obtained.

Sources of Information--

The costs presented in this report are derived from cost information in existing published sources and also from recent vendor information. It is the objective of this effort to present cost levels for phosgene process and storage facilities using the best costs for available sources. The primary sources of cost information are Peters and Timmerhaus (37), Chemical Engineering (49), and Valle-Riestra (50) supplemented by other sources and references where necessary. Adjustments were made to update all costs to a June 1986 dollar basis. In addition, for some equipment items, well-documented costs were not available and they had to be developed from component costs.

TABLE 5-28. FORMAT FOR TOTAL ANNUAL COST

Item No.	Item	Cost
1	Total Direct Cost	-
2	Capital Recovery on Equipment Items[a]	0.163 x Item 1
3	Maintenance Expense on Equipment Items	0.01 x Item 1
4	Total Procedural Items	-
5	Total Annual Cost	Items (2 + 3 + 4)

[a]Based on a recovery factor at 10% cost of capital for 10 years.

Costs in this document reflect the "typical" or "average" representation for specific equipment items. This restricts the use of data in this report to:

- Preliminary estimates used for policy planning;
- Comparison of relative costs of different levels or systems; and
- Approximations of costs that might be incurred for a specific application.

The costs in this report are considered to be "order of magnitude" with a ±50 percent margin. This is because the costs are based on preliminary estimates and many are updated from literature sources. Large departures from the design basis of a particular system presented in this manual or the advent of a different technology might cause the system cost to vary by a greater extent than this. If used as intended, however, this document will provide a reasonable source of preliminary cost information for the facilities covered.

When comparing costs in this manual to costs from other references, the user should be sure the design bases are comparable and that the capital and annual costs as defined here are the same as the costs being compared.

Cost Updating--

All costs in this report are expressed in June 1986 dollars. Costs reported in the literature were updated using cost indices for materials and labor.

Costs expressed in base year dollars may be adjusted to dollars for another year by applying cost indices as shown in the following equation:

$$\text{New base year cost} = \text{old base year cost} \times \frac{\text{new base year index}}{\text{old base year index}}$$

The Chemical Engineering (CE) Plant Cost Index was used in updating cost for this report. For June 1986, the index is 316.3.

Equipment Costs--

Most of the equipment costs presented in this manual were obtained directly from literature sources of vendor information and correspond to a specific design standard. Special cost estimating techniques, however, were used in determining the costs associated with vessels, piping systems, scrubbers, diking, and enclosures. The techniques used are presented in the following subsections of this manual.

Vessels--The total purchased cost for a vessel, as dollars per pound of weight of fabricated unit free-on-board based freight (f.o.b.) with carbon steel as the basis (January 1979 dollars), were determined using the following equation from Peters and Timmerhaus (37):

$$\text{Cost} = [50(\text{Weight of Vessel in Pounds})^{-0.34}]$$

The vessel weight is determined using appropriate design equations as given by Peters and Timmerhaus (37) which allow for wall thickness adjustments for corrosion allowances, for example. The vessel weight is increased by a factor of 0.15 for horizontal vessels and 0.20 for vertical vessels to account for the added weight due to nozzles, manholes, and skirts or saddles. Appropriate factors are applied for different materials of construction as given in Peters and Timmerhaus (37). The vessel costs are updated using cost factors. Finally a shipping cost amounting to 10 percent of the purchased cost is added to obtain the delivered equipment cost.

Piping--Piping costs were obtained using cost information and data presented by Yamartino (41). A simplified approach is used in which it is assumed that a certain length of piping containing a given number of valves, flanges, and fittings is contained in the storage or process facility. The data presented by Yamartino (41) permit cost determinations for various

lengths, sizes, and types of piping systems. Using these factors, a representative estimate can be obtained for each of the storage and process facilities.

Diking--Diking costs were estimated using Mean's Manual (46) for reinforced concrete walls. The following assumptions were made in determining the costs. The dike contains the entire contents of a tank in the event of a leak or release. Two dike sizes are possible: a three-foot high dike, six-inches thick and a top-of-tank height dike ten-inches thick. The tanks are raised off the ground and are not volumetrically included in the volume enclosed by the diking. These assumptions facilitate cost determination for any size diking system.

Enclosures--Enclosure costs were estimated using Mean's Manual (46) for both reinforced concrete and steel-walled buildings. the buildings are assumed to enclose the same area and volume as the top-of-tank height dikes. The concrete building is ten inches thick with a 26-gauge steel roof and a metal door. The steel building has 26 gauge roofing and siding and metal door. The cost of a ventilation system was determined using a typical 1,000 scfm unit and doubling the cost to account for duct work and requirements for the safe enclosure of hazardous chemicals.

Scrubbers--Scrubber costs were estimated using the following equation for spray towers based on the actual cubic feet per minute of flow at a chamber velocity of 600 feet/minute (48):

$$\text{Costs} = 0.235 \times (\text{ACFM} + 43{,}000)$$

A release rate of 10,000 ft^3/minute was assumed for the storage vessel systems and an appropriate rate was determined for process system based on the quantity of hazardous chemicals present in the system at any one time. For the polycarbonate reactor system, a release rate of 1,000 ft^3/minute was assumed. In addition to the spray tower, the costs also include pumps and a storage tank for the scrubbing medium. The costs presented are updated to June 1986 dollars.

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Installation Factors--

Installation Costs were developed for all equipment items included in both the process and storage systems. The costs include both the material and labor costs for installation of a particular piece of equipment. The costs were obtained directly from literature sources and vendor information or indirectly by assuming a certain percentage of the purchased equipment cost through the use of estimating factors obtained from Peters and Timmerhaus (37) and Valle-Riestra (50). Table 5-29 lists the cost factors used or the reference from which the cost was obtained directly. Many of the costs obtained from the literature were updated to June 1986 dollars using a 10 percent per year rate of increase for labor and cost indices for materials associated with installation.

TABLE 5-29. FORMAT FOR INSTALLATION COSTS

Equipment Item	Factor or Reference
Vessels:	
Storage Tank	0.45
Expansion Tank	0.25
Piping and Valves:	
Pipework	Ref. 41
Expansion Loop	Ref. 37
Reduced Pressure Device	Ref. 37
Check Valves	Ref. 37
Gate Valves	Ref. 37
Ball Valves	Ref. 37
Excess Flow Valves	Ref. 37
Angle Valves	Ref. 37
Relief Valves	Ref. 37
Rupture Disks	Ref. 30
Process Machinery:	
Centrifugal Pump	0.43
Gear Pump	0.43
Instrumentation:	
All Instrumentation Items	0.25
Enclosures:	Ref. 46
Diking:	Ref. 46
Scrubbers:	0.45

SECTION 6

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APPENDIX A

GLOSSARY

This glossary defines selected terms used in the text of this manual which might be unfamiliar to some users or which might be used differently by different authors.

Accidental release: The unintentional spilling, leaking, pumping, purging, emitting, emptying, discharging, escaping, dumping, or disposing of a toxic material into the environment in a manner that is not in compliance with a plant's federal, state, or local environmental permits and results in toxic concentrations in the air that are a potential health threat to the surrounding community.

Assessment: The process whereby the hazards that have been identified are evaluated in order to estimate the level of risk.

Containment/control: A system to which toxic emissions from safety relief discharges are routed to be controlled. A caustic scrubber and/or flare can be containment/control devices. These systems may serve the dual function of destructing continuous process exhaust gas emissions.

Electromotive Series of Metals: A list of metals and alloys arranged according to their standard electrode potentials, which also reflect their relative corrosion potential.

Enthalpy: A thermodynamic property of a chemical related to its energy content at a given condition of temperature, pressure, and physical state. Enthalpy is the internal energy added to the product of pressure times volume.

Numerical values of enthalpy for various chemicals are always based on the change in enthalpy from an arbitrary reference pressure and temperature and physical state, since the absolute value cannot be measured.

Facility: A location at which a process or set of processes is used to produce, refine or repackage chemicals, or a location where a large enough inventory of chemicals is stored so that a significant accidental release of a toxic chemical is possible.

Hazard: A source of danger. The potential for death, injury or other forms of damage to life and property.

Identification: The recognition of a situation, its causes, and consequences relating to a defined potential, e.g. Hazard Identification.

Mild steel: Carbon steel containing a maximum of about 0.25% carbon. Mild steel is satisfactory for use where severe corrodants are not encountered or where protective coatings can be used to prevent or reduce corrosion rates to acceptable levels.

Mitigation: Any measure taken to reduce the severity of the adverse effects associated with the accidental release of a hazardous chemical.

Passivation film: A layer of oxide or other chemical compound of a metal on its surface that acts as a protective barrier against corrosion or further chemical reaction.

Plant: A location at which a process or set of processes is used to produce, refine, or repackage, chemicals.

Prevention: Design and operating measures applied to a process to ensure that primary containment of toxic chemicals is maintained. Primary containment means confinement of toxic chemicals within the equipment intended for normal operating conditions.

Primary Containment: The containment provided by the piping, vessels, and machinery used in a facility for handling chemicals under normal operating conditions.

Probability/potential: A measure, either qualitative or quantitative, that an event will occur within some unit of time.

Process: The sequence of physical and chemical operations for the production, refining, repackaging, or storage of chemicals.

Process machinery: Process equipment, such as pumps, compressors, heaters, or agitators, that would not be categorized as piping and vessels.

Protection: Measures taken to capture or destroy a toxic chemical that has breached primary containment, but before an uncontrolled release to the environment has occurred.

Qualitative Evaluation: Assessing the risk of an accidental release at a facility in relative terms, the end result of the assessment being a verbal description of the risk.

Quantitative Evaluation: Assessing the risk of an accidental release at a facility in numerical terms, the end result of the assessment being some type of number reflects risk, such as faults per year or mean time between failure.

Reactivity: The ability of one chemical to undergo a chemical reaction with another chemical. Reactivity of one chemical is always measured in reference to the potential for reaction with itself or with another chemical. A chemical is sometimes said to be "reactive", or have high "reactivity", without reference to another chemical. Usually this means that the chemical has the ability to react with common materials such as water, or common materials of construction such as carbon steel.

Redundancy: For control systems, redundancy is the presence of a second piece of control equipment where only one would be required. The second piece of equipment is installed to act as a backup in the event that the primary piece of equipment fails. Redundant equipment can be installed to back up all or selected portions of a control system.

Risk: The probability that a hazard may be realized at any specified level in a given span of time.

Secondary Containment: Process equipment specifically designed to contain material that has breached primary containment before the material is released to the environment and becomes an accidental release. A vent duct and scrubber attached to the outlet of a pressure relief device are examples of secondary containment.

Toxicity: A measure of the adverse health effects of exposure to a chemical.

APPENDIX B

TABLE B-1. METRIC (SI) CONVERSION FACTORS

Quantity	To Convert From	To	Multiply By
Length:	in	cm	2.54
	ft	m	0.3048
Area:	in^2	cm^2	6.4516
	ft^2	m^2	0.0929
Volume:	in^3	cm^3	16.39
	ft^3	m^3	0.0283
	gal	m^3	0.0038
Mass (weight):	lb	kg	0.4536
	short ton (ton)	Mg	0.9072
	short ton (ton)	metric ton (t)	0.9072
Pressure:	atm	kPa	101.3
	mm Hg	kPa	0.133
	psia	kPa	6.895
	psig	kPa*	(psig+14.969) x 6.895
Temperature	°F	°C*	(5/9)x(°F-32)
	°C	K*	°C+273.15
Caloric Value; Enthalpy:	Btu/lb	kJ/kg	2.326
	Btu/lbmol	kJ/kgmol	2.326
	kcal/gmol	kJ/kgmol	4.184
Specific-Heat Capacity:	Btu/lb-°F	kJ/kg-°C	4.1868
Density:	lb/ft^3	kg/m^3	16.02
	lb/gal	kg/m^3	119.8
Concentration:	oz/gal	kg/m^3	
	quarts/gal	cm^3/m	25,000
Flowrate:	gal/min	m^3/min	0.0038
	gal/day	m^3/day	0.0038
	ft^3/min	m^3/min	0.0283
Velocity:	ft/min	m/min	0.3048
	ft/sec	m/sec	0.3048
Viscosity:	centipoise (CP)	Pa-s(kg/m-s)	0.001

*Calculate as indicated.